

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM

PROCEEDINGS

VOLUME XXXII

No. 7

President: F. A. F. C. WENT

Secretary: B. BROUWER

CONTENTS

- F. A. H. SCHREINEMAKERS: "Membrane and Osmosis". I, p. 837.
- E. H. REERINK and A. VAN WIJK: "On the photochemical reactions of ergosterol."
(Communicated by Prof. G. HOLST), p. 845.
- H. G. BUNGENBERG DE JONG and H. R. KRIJYT: "Coacervation. (Partial miscibility in colloid systems)". (Preliminary Communication), p. 849. (With one plate).
- H. R. KRIJYT: "Die ungleichmässige Verteilung der stabilisierenden Faktoren über die Oberfläche kolloider Teilchen", p. 857.
- W. H. KEESOM, SOPHUS WEBER and G. NØRGAARD: "New measurements on the vapour pressure curve of liquid helium". I, p. 864.
- W. J. DE HAAS and J. VOOGD: "Disturbance of the superconductivity of the compound Bi_2Tl_3 and of the alloys $Sn-Sb$ and $Sn-Cd$ by magnetic fields", p. 874.
- P. EHRENFEST und A. J. RUTGERS: "Zur Thermodynamik und Kinetik der thermoelektrischen Erscheinungen in Krystallen, insbesondere des BRIDGMAN-Effektes". II, p. 883.
- C. WINKLER: "Preface to Volume II of the microscopical atlas of the human brain", p. 894. (With 6 plates).
- G. VAN RIJNBERK and Miss L. KAISER: "Experimental contributions to the knowledge concerning the segmental innervation of the abdominal muscles in the dog. (3rd communication). The M. obliquus internus, the M. transversus abdominis and conclusions", p. 899.
- W. A. P. SCHÜFFNER, P. C. KORTEWEG and N. H. SWELLENGREBEL: "Experimental malaria with protracted incubation", p. 903.
- A. KRUPKOWSKI and W. J. DE HAAS: "The properties of the $Ni-Cu$ alloys at low temperatures", p. 912.
- A. KRUPKOWSKI and W. J. DE HAAS: "Thermo-electric and dilatation determinations with $Ni-Cu$ alloys at low temperatures", p. 921.
- W. F. GISOLF: "The rocks of the Katmai Region (Alaska)", p. 930.

- H. DE JONG et H. BARUK: "Etudes sur la catatonie expérimentale. I. L'épreuve de la bulbocapnine chez la grenouille et la souris". (Communicated by Prof. B. BROUWER), p. 940. (With one plate).
- H. BARUK et H. DE JONG: "Etudes sur la catatonie expérimentale. II. L'épreuve de la bulbocapnine chez la poule. Catalepsie et sommeil". (Communicated by Prof. B. BROUWER), p. 947. (With one plate).
- A. SMITS: "Die Pseudo-komponenten des Wasserstoffs". II. (Communicated by Prof. P. ZEEMAN), p. 951.
- W. J. C. VERHAART: "Some Clinical and Anatomical Observations on the "Paraplegie en Flexion" and Related Motor Disturbances", (Communicated by Prof. B. BROUWER), p. 961. (With one plate).
- WILLEMINA M. COELINGH: "Aggregation-substance in the terminal glands of *Drosera*" (Communicated by Prof. F. A. F. C. WENT), p. 973.
- J. W. A. VAN KOL: "Zwei Kongruenzen von biquadratischen Raumkurven zweiter Art". (Communicated by Prof. HENDRIK DE VRIES), p. 978.
- M. A. VAN HERWERDEN: "Reversible changes in the epithelium of the tadpole. A test for differences in permeability caused by energy of radiation". (Communicated by Prof. J. BOEKE), p. 985.
- C. B. BIEZENO: "Ueber eine Stabilitätsfrage beim gelenkig gelagerten, schwach gekrümmten Stabe". (Communicated by Prof. W. VAN DER WOUDE), p. 990.
- M. J. VAN UVEN: "Skew Correlation between three and more Variables". II. (Communicated by Prof. A. A. NIJLAND), p. 995.
- T. H. VAN DEN HONERT: "Studies on Limiting Factors in Carbon Dioxide Assimilation". (Communicated by Prof. F. A. F. C. WENT), p. 1008.
- Corrigendum, p. 1022.
- Erratum, p. 1022.
-

(Communicated at the meeting of September 28, 1929).

Introduction.

In previous communications¹⁾ we have described the phenomena obtaining with the osmosis of one or more substances, with the aid of the O. A. (Osmotic-Attraction) of the two liquids; follows the question whether these phenomena may also be explained with the aid of the absorption of the membrane; before discussing this question however, we shall first enter upon a brief survey of this absorption.

We represent the various substances of which a membrane consists, before it has absorbed any other substances, by a single letter Q . If we have a membrane $M(W)$ i.e. a membrane absorbing water only, its composition, when this membrane will have absorbed water, may be represented by:

$$1 \text{ gr } Q + w \text{ mol (gr) } W \dots \dots \dots (1)$$

i.e. by the number of mols (or grams) of water absorbed by 1 gr. of Q ; we shall call w the W -amount of this membrane.

If this dry membrane is put into a liquid from which it takes water, its W -amount will first increase more rapidly and later on more slowly, until it will finally change no more and the membrane is saturated with water (we shall refer to this later on). We then have a system:

$$L + M(W) \dots \dots \dots (2)$$

in which the two phases are in equilibrium; with every composition of liquid L then goes a definite W -amount of the membrane; in order to enable us to describe some phenomena later on in a more simple way, we shall say that liquid L gives this W -amount to the membrane, or that the membrane obtains this W -amount in the liquid L .

Binary liquids and a membrane $M(W)$.

In system (2) we now take for L a binary liquid, containing the substances $W + X$; we represent this in the usual way by a point of line WX (figs. 1—4).

¹⁾ Verslagen Kon. Akademie Amsterdam, 36, 779, 987, 1103, 1218 (1927); 37, 374, 634, 849 (1928).

These Proceedings, 30, 761, 934, 1095, 1106 (1927); 31, 459, 811, 923 (1928); 32, 23, 254 (1929).

We now represent the W -amount given to the membrane by a liquid a_1 , by point w_1 i.e. by the length of the line a_1w_1 , intersecting WX perpendicularly.

We now imagine that the liquid gets every possible composition, so that it will be represented successively by all points of WX ; as a definite W -amount goes with every liquid, the point representing this W -amount will travel along a curve; we shall call it the W -curve of the membrane. We may imagine this to be represented in figs. 1 and 3 by the fully-drawn curve $W'X$.

Point w_2 (viz. the length of line a_2w_2) consequently represents the W -amount given to the membrane by liquid a_2 ; point W' represents the W -amount the membrane gets in pure water; etc. Point X represents a liquid consisting of substance X only; as consequently the membrane cannot absorb water here either and its W -amount must therefore be zero, the W -curve must also run through point X .

If the composition of the liquid in system (2) is changed, the membrane will generally also change its W -amount; we now may deduce:

A_1 . if water is added to the liquid, the membrane $M(W)$ will also absorb water; consequently its W -amount will increase;

A_2 . if water is taken from the liquid, the membrane $M(W)$ will also give out water; so its W -amount will become smaller.

As we shall see later on, however, this obtains only for a membrane $M(W)$; for it does not obtain any longer, as soon as the membrane, besides water, absorbs one or more other substances too.

We now apply this to liquid a_1 of fig. 1. When water is added, this liquid will travel along line a_1W , starting from a_1 going to W ; so the W -amount of the membrane must increase from w_1 as far as point W' . If water is taken from liquid a_1 , this liquid will travel along line a_1X from a_1 to X ; then the W -amount of the membrane must decrease from w_1 as far as X . So the W -curve must descend continually from point W as far as point X . We shall call such a curve, showing neither a maximum nor a minimum "monotonous". Then we may say:

B . the W -curve of a membrane $M(W)$ is a monotonous curve.

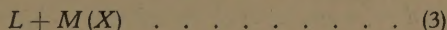
When deducing the W -curve we have assumed that X is a liquid; if X is a solid, however, one of the liquids will be saturated with solid X . If this should be the liquid a_2 for instance, w_2 will represent the W -amount the membrane will get in the liquid saturated with X ; part w_2X of the W -curve will then represent metastable conditions, viz. the W -amount the membrane would get in supersaturated liquids.

It would also be possible to imagine a hydrate of X occurring as a solid, or an unmixing in two liquids; it does not serve our purpose, however, to discuss this here.

Binary liquids and a membrane $M(X)$.

Every thing that has been said above of a membrane $M(W)$ obtains

for any other membrane absorbing one substance only. If we have e.g. the system :



in which the membrane absorbs only the substance X , we may represent the composition of the membrane by :



Instead of A_1 and A_2 we now have :

C_1 . when X is added to the liquid, the membrane $M(X)$ will also absorb X ;

C_2 . if X is taken from the liquid, the membrane $M(X)$ will also give out X .

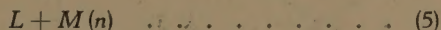
Instead of B we have :

D . the X -curve of a membrane $M(X)$ is a monotonous curve.

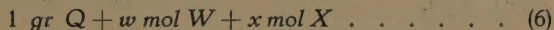
We may imagine this X -curve to be represented in figs. 1 and 2 by the dotted curve WX' ; so the membrane will get an X -amount $= a_1x_1$ in the liquid a_1 , an X -amount $= a_2x_2$ in the liquid a_2 ; etc.

Binary liquids and a membrane $M(n)$.

We now take a system :



in which the membrane absorbs the two substances W and X ; we may then represent the composition of this membrane by :



If for instance the membrane is put into the liquid a_1 (figs. 1—4) we get a definite W - and X -amount in it; we once more represent this W -amount by a point w_1 and the X -amount by a point x_1 .

If we now suppose that the liquid travels along line WX , we get two curves; we shall call them the W - and the X -curve of the membrane $M(n)$.

So the membrane $M(n)$ has a W - as well as an X -curve, whereas a membrane $M(W)$ has a W -curve only, and a membrane $M(X)$ an X -curve only. The W - and X -curves of a membrane $M(n)$ however, are different curves and may have a shape differing greatly from that of the W -curve of a membrane $M(W)$ and the X -curve of a membrane $M(X)$. These two curves namely, are always monotonous, as has already been stated in B and D ; this does not always obtain any longer however for the W - and X -curves of a membrane $M(n)$. We now may distinguish the following cases :

- E_1 . both curves are monotonous (fig. 1);
- E_2 . the W -curve has a maximum; the X -curve is monotonous (fig. 2);
- E_3 . the W -curve is monotonous; the X -curve has a maximum (fig. 3);
- E_4 . both curves have a maximum (fig. 4);
- E_5 . in one curve or in both curves we find besides a maximum also a minimum.

If we have a membrane for which E_1 obtains, we may imagine the W - and X -curves to be represented by fig. 1. The shape of these curves shows :
if more and more of the substance X is continually added to the water, the W -amount of the membrane will decrease and its X -amount increase continually.

In our next paper we shall discuss an example.

If we have a membrane, for which E_2 obtains, fig. 2 may represent the W - and the X -curve ; the W -curve here has a maximum in H_w .

If we suppose $a_4 w_4 = WW'$, the membrane will get the same

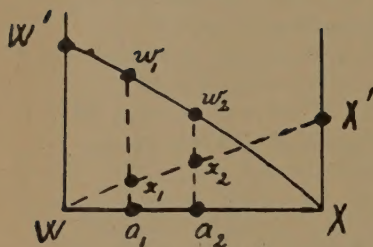


Fig. 1.

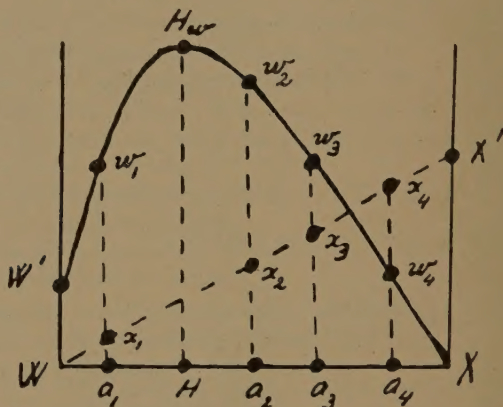


Fig. 2.

W -amount in the liquid a_4 as in pure water ; all liquids situated between W and a_4 give a larger-, all liquids situated between a_4 and X a smaller W -amount to the membrane than the pure water ; the liquid H gives the largest W -amount to the membrane. This shows :

if more and more X is continually added to the water, the W -amount of the membrane will begin by increasing, will reach a maximum, and decrease afterwards ; its X -amount will increase continually.

In our next paper we shall discuss an example.

Fig. 3 represents the W - and X -curves of a membrane, for which E_3 obtains ; the X -curve here has a maximum in the point U_x . We now see :

if more and more X is continually added to the water, the W -amount of the membrane will continually decrease ; its X -amount will begin by increasing, reach a maximum and decrease afterwards.

We now take a membrane, for which E_4 obtains ; both curves then have a maximum ; this has been represented in fig. 4. The two maxima

H_w and U_x cannot be situated arbitrarily with respect to each other; for if a liquid travels along line WX from W to X , the W -curve will be the

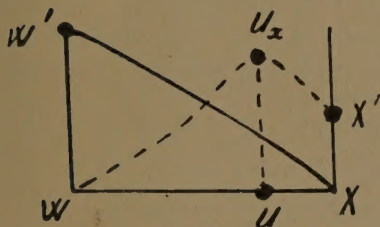


Fig. 3.

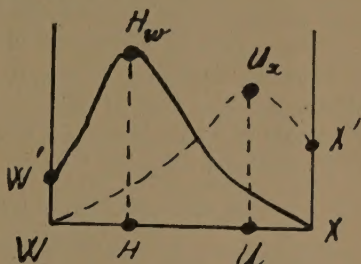


Fig. 4.

first to reach its maximum, followed by the X -curve. So when the membrane reaches its maximum W -amount, its X -amount will go on increasing; when it reaches its maximum X -amount, its W -amount will consequently decrease.

In our next paper we shall discuss an example.

If we have a membrane for which E_5 obtains, a minimum will occur in one curve or in both curves; it is clear that no minimum is possible without a maximum; we are not going to enter upon a discussion of this subject here.

Perhaps we might be inclined to believe now, that the W - and the X -curve may be situated quite arbitrarily with respect to one another, so that also the W - and the X -amount of the membrane might vary arbitrarily with respect to each other; this is not the case however.

To prove this we take an osmotic system:

$$n \times L + M \quad \dots \quad (7)$$

consisting of n quantities of a liquid L and of one quantity of a membrane. We shall call it system S . We represent the composition of L and M by:

$$x \text{ mol } X + (1 - x) \text{ mol } W \quad \dots \quad (8)$$

$$1 \text{ gr } Q + x_0 \text{ mol } X + w_0 \text{ mol } W \quad \dots \quad (9)$$

We may now represent the total composition of this system S by:

$$1 \text{ gr } Q + (nx + x_0) \text{ mol } X + [n(1 - x) + w_0] \text{ mol } W \quad \dots \quad (10)$$

We now take a second system:

$$(n + dn) \times L' + M' \quad \dots \quad (11)$$

which we shall call S' . We suppose there is only a minute difference

between L' and M' and L and M of system S ; we may represent the composition of L' and M' by:

$$(x + dx) \text{ mol } X + (1 - x - dx) \text{ mol } W \quad \quad (12)$$

$$1 \text{ gr } Q + (x_0 + dx_0) \text{ mol } X + (w_0 + dw_0) \text{ mol } W \quad . . . \quad (13)$$

in which dx , dx_0 and dw_0 are very small; dw_0 then is the change of the W -amount, dx_0 that of the X -amount of the membrane, when the X -amount of the liquid changes with dx .

We now may represent the total composition of this system S' by:

$$\left. \begin{aligned} 1 \text{ gr } Q + [(n + dn)(x + dx) + x_0 + dx_0] \text{ mol } X + \\ + [(n + dn)(1 - x - dx) + w_0 + dw_0] \text{ mol } W \end{aligned} \right\} \quad . \quad (14)$$

We now have the well-known theorem:

if two systems have the same total compositions, so that the one may change into the other, one of these systems is metastable or labile with respect to the other; the system having the smaller thermodynamical potential when temperature and pressure are constant, is the stabler of the two.

If we now suppose the W - and the X -curve to represent systems, stable with respect to each other, it must not be possible for the systems S and S' to change into each other; the total compositions of the two systems consequently must be different. Follows that the two equations:

$$nx + x_0 = (n + dn)(x + dx) + x_0 + dx_0 \quad \quad (15)$$

$$n(1 - x) + w_0 = (n + dn)(1 - x - dx) + w_0 + dw_0 \quad . . \quad (16)$$

expressing that the systems S and S' have the same compositions, (compare 10 and 14) are not valid.

If $dn \cdot dx$, which is infinitely small with respect to dn and dx , is neglected, we find:

$$0 = x \, dn + n \, dx + dx_0 \quad \quad (17)$$

$$0 = (1 - x) \, dn - n \, dx + dw_0 \quad \quad (18)$$

After elimination of dn follows:

$$n \, dx = x \, dw_0 - (1 - x) \, dx_0 \quad \quad (19)$$

To n in system S every possible value may be given between 0 and $+\infty$; if dx is taken positive, the same must obtain for $n \, dx$. So it will only then be impossible to satisfy (19) when the second term is always negative; so dw_0 and dx_0 must satisfy:

$$x \, dw_0 - (1 - x) \, dx_0 \quad \quad (20)$$

a relation we can also deduce in an other way. This makes it clear that the W - and X -amounts of a membrane cannot change arbitrarily; for these changes must satisfy (20).

If only the signs of dw_0 and dx_0 are heeded, we may imagine the four cases of table I; if besides we suppose $dw_0 = 0$, or $dx_0 = 0$, we may also imagine the four cases of table II. As however, dw_0 and dx_0 must satisfy (20) these cases will not all of them be possible.

TABLE I.

| | dw_0 | dx_0 |
|----|--------|----------|
| a. | + | +(cond.) |
| b. | - | + |
| c. | - | -(cond.) |
| d. | [+] | [-] |

TABLE II.

| | dw_0 | dx_0 |
|----|--------|--------|
| e. | 0 | + |
| f. | - | 0 |
| g. | [0] | [-] |
| h. | [+] | [0] |

If for instance we suppose: $dw_0 = \text{pos.}$, it will only be possible to satisfy (20) by $dx_0 = \text{pos.}$ (case a); case h, viz. $dx_0 = 0$ and case d, viz. $dx_0 = \text{neg.}$ are impossible.

If we suppose $dw_0 = 0$, dx_0 must be pos. (case e); so case g viz. $dx_0 = \text{neg.}$ is impossible.

If we suppose $dw_0 = \text{neg.}$ (20) may be satisfied by $dx_0 = \text{pos.}$ (case b), by $dx_0 = \text{neg.}$ (case c) and by $dx_0 = 0$ (case f).

In table I we find with case a between brackets "cond." i.e. "condition"; the meaning of this is that a does not obtain for all arbitrary pos. values of dw_0 and dx_0 , but only for those pos. values, satisfying a certain condition, viz. (20). The same obtains in c for the neg. values of dw_0 and dx_0 .

We now write down (20) in this way:

$$\frac{dw_0}{dx} < \frac{1-x}{x} \cdot \frac{dx_0}{dx} \dots \dots \dots (21)$$

Here dw_0/dx is the direction of the tangent in a point of the W-curve and dx_0/dx the direction of the tangent in the corresponding point of the X-curve. If we take e.g. the liquid a_1 (compare the preceding figures) dw_0/dx will determine the direction of the tangent in point w_1 of the W-curve and dx_0/dx the direction of the tangent in point x_1 of the X-curve.

If, as will always be our practice in future, we follow a curve to the right, we shall find: the W-curve rises when dw_0/dx is pos.; it falls when dw_0/dx is neg.; it has a horizontal tangent, when dw_0/dx is zero.

The direction of the X-curve of course, is determined in a similar way by dx_0/dx .

If we imagine a rising direction of a curve indicated by the sign \uparrow , a falling one by \downarrow and a horizontal tangent by $-$, the eight cases of tables III and IV may be imagined. These tables follow at once from tables I and II; for it is clear that the signs \uparrow and $+$, signs \downarrow and $-$ and signs $-$ and 0 agree.

In fig. 1 only case b is found viz. an ever falling W- and a rising X-curve.

In fig. 2 *a*, *b* and the transition-case *e* are found. For all liquids between *W* and *H* namely, the two curves rise (case *a*) ; for all liquids between

TABLE III.

| | <i>W</i> -curve | <i>X</i> -curve | |
|-----------|-----------------|-----------------|---------|
| <i>a.</i> | ↑ | ↑ | (cond. |
| <i>b.</i> | ↓ | ↑ | |
| <i>c.</i> | ↓ | ↓ | (cond.) |
| <i>d.</i> | [↑ | ↓] | |

TABLE IV.

| | <i>W</i> -curve | <i>X</i> -curve |
|-----------|-----------------|-----------------|
| <i>e.</i> | — | ↑ |
| <i>f.</i> | ↓ | — |
| <i>g.</i> | [— | ↓] |
| <i>h.</i> | [↑ | —] |

H and *X* the *W*-curve will fall, the *X*-curve rise (case *b*) ; for liquid *H* the *W*-curve has a horizontal tangent and the *X*-curve will rise (case *e*).

In fig. 3 the cases *b*, *c* and the transition-case *f* are found ; in fig. 4 all cases are found these tables have shown to be possible.

Table IV proves that the *X*-curve must rise, when the *W*-curve has a maximum (case *e*), and that the *W*-curve must fall when the *X*-curve has a maximum ; figures 2, 3 and 4 agree with this. The cases *d*, *g* and *h* which have been shown to be impossible, do not occur in the figures.

(To be continued.)

Leiden, Lab. of Inorg. Chemistry.

Physics. — *On the photochemical reactions of ergosterol.* By E. H. REERINK and A. VAN WIJK. (Communicated by Prof. G. HOLST.)

(Communicated at the meeting of September 28, 1929).

In the course of the last years, the photochemical conversion of ergosterol has aroused a great deal of interest. This is mainly due to one of the substances that are formed during the mentioned reaction, the vitamin-D, which is of high importance in medicine and biology.

According to our view insufficient attention has been paid to the influence of the wavelength used for the irradiation. Researches concerning this question were made in collaboration with Prof. Dr. W. STORM VAN LEEUWEN and his co-workers Messrs. J. W. R. EVERSE and J. VAN NIEKERK, who charged themselves with the biological part. It appeared already from preliminary experiments, in which light-sources of different energydistribution over the wavelengths were used, that the course of the reaction depends on this distribution. By a systematical research we arrived at the conception that there exist two wavelength-ranges which have a typically different action on the ergosterol, see Fig. 1,

1. the wavelength-range $300 \mu\mu > \lambda > 270 \mu\mu$ ("longwave" range)
2. the wavelength-range at about $250 \mu\mu$ ("shortwave" range)

By means of suitably selected light-sources and filters it was possible to realise irradiations, with each of these wavelength-ranges without light of the other range. For the purpose of irradiation the ergosterol was solved in hexane and brought into an all-quartz cuvette, which was evacuated and then sealed-off. The progress of the reaction was studied by means of the determination of the absorption-spectrum of the liquid in the cuvette. For this determination we choose the method of photographic measurement of light-intensities, as worked out in the Physical Laboratory of Utrecht, under the direction of Prof. Dr. L. S. ORNSTEIN. A tube emitting the continuous hydrogen-spectrum was used as a lightsource.

It appeared, that during the first period of the reaction (in which less than about 60 % of the ergosterol had been converted) caused by longwave irradiation, the absorption-spectra can be interpreted by the assumption, that besides the ergosterol only one single substance is present. The absorption-spectrum of this reaction-product has been established in two different manners, which gave well agreeing results :

10. By means of digitonine the amount of unchanged ergosterol present in an irradiated solution, was determined. The absorption due to this ergosterol was subtracted from that of the solution, determined before; the remaining absorption was then calculated for a solution of the reaction-

product of a fixed concentration. In case the conversion of the solution used for the determination did not exceed about 60 % the spectrum calculated in the above manner was independent on the degree of conversion.

20. The absorption-spectrum of an irradiated solution, after precipitation of the unchanged ergosterol by means of digitonine was directly measured. This method, though being the most obvious way to determine the absorption of the reaction-product, is only mentioned in the second place, as it appears to be very difficult to perform all necessary operations under such circumstances as are required by the great sensitiveness of the product for oxygen.

Only by the fact that the product separated by us, shows an absorption-spectrum which totally agrees with that calculated in the first-mentioned manner we can be certain that we have succeeded in preparing the unchanged reaction-product.

The absorption-spectrum shows a broad band with a maximum at about 265μ and a height that is of the same order of magnitude as the maximum-height of the ergosterol-curve, see Fig. 2.

From the experiments of Messrs. EVERSE and VAN NIEKERK, which are for the moment still in progress with a great number of animals, it follows that the antirachitic activity of longwave-irradiated ergosterol goes parallel with the presence of the above mentioned first reaction-product and that the activity of this product is the highest that has been found till now. *This proves the identity of this substance with the vitamine-D.*

We were able to obtain the vitamin-D in a crystallised state: the crystals form lozengeshaped transparant plates which melt below 0°C . to a colourless vitreous mass.

The absorption-curves of solutions irradiated for a longer time can no more be calculated from those of ergosterol and vitamin-D. In this following stage of the reaction the photochemical conversion of the first reaction-pro-

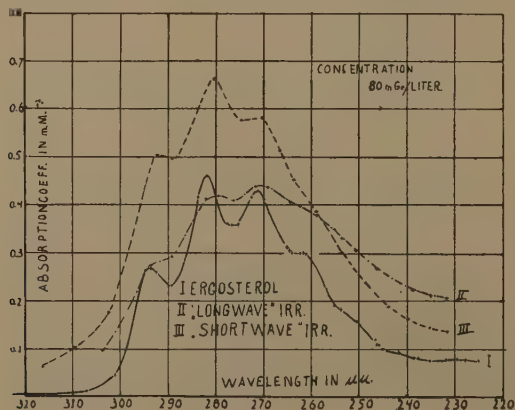


Fig. 1.

duct itself becomes appreciable, which is shown by a progressive decrease of the absorption in the range from 300—260 $\mu\mu$ (Fig. 3 shows the spectrum of the final substance formed by longwave-irradiation (curve I) in comparison with that of the final state formed by shortwave-irradiation, c.f. furtheron.)

From the absorption-curves of the irradiated solutions, it is obvious that upon shortwave irradiation the course of the reaction is totally different from that upon longwave-irradiation (See fig. 1 in which the curve I

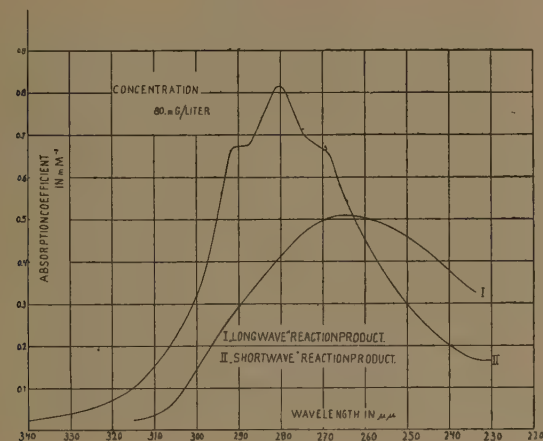


Fig. 2.

represents the absorption-spectrum of unirradiated, curve II that of longwave-irradiated, and curve III that of shortwave-irradiated ergosterol). While upon longwave-irradiation the total absorption does not change very much during a great part of the process, upon shortwave-irradiation it increases very quickly in the beginning, attains a maximum of about twice the original value and then decreases slowly till almost no absorption is left. In this case it appears impossible to describe the first stage of the reaction in such a simple manner as before. As the absorption-curves calculated from those of the irradiated solutions after subtraction of the absorption of the unchanged ergosterol (determined with digitonine) depend much on the degree of conversion of the solutions, it is certain that now more than one new substance has been formed. In the second stage however, after the absorption has passed its maximum, we found that the absorption-curves of solutions irradiated during increasing times, show decreasing but proportional heights, over a great range of wavelengths. This proves that in this stage of the reaction one single absorbing substance is gradually converted into a substance with low specific absorption. These results suffice to determine the form, but not the absolute magnitude of the absorption-curve of the reaction-product present in the beginning of the

second stage. (See fig. 2 which gives this absorption-spectrum, curve II, in comparison to the curve of the vitamin-D, curve I.)

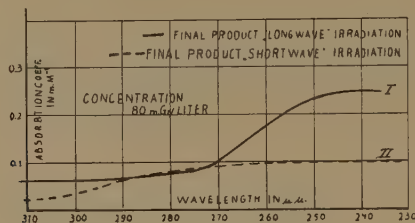


Fig. 3.

Now it appears that the absorption-curves in the first stage can be calculated in the assumption, that, besides the ergosterol, this shortwave reaction-product and vitamin-D are present. One finds that after a very short time the formed amount of vitamin-D reaches a maximum of at most 15 % of the original quantity of ergosterol and then decreases quickly, whereas the amount of the other product increases gradually till the reaction comes into the second stage. The biological experiments which can check these hypotheses, as far as the vitamin-D contents is concerned, are not in contradiction herewith, but are still in progress in order to permit us to draw definitive conclusions.

It follows from our research, that for the formation of vitamin-D the wavelength of the used light is of great importance. While by the use of light of wavelength between 300 and 270 $\mu\mu$ up to about 60 % of the ergosterol can be converted into vitamin-D *without the formation of by-products*, it is impossible to obtain more than a yield of about 15 % by the use of light of wavelength 254 $\mu\mu$, in which case *the formation of by-products cannot be prevented*. It will be necessary to pay attention to this point in case a standard for the irradiation will be chosen.

It has further become possible to determine the vitamin-D contents of irradiated ergosterol-solutions in a physical way, as the absorption-spectrum of the vitamin and the other occurring substances are established. The biological experiments show that the activity of this vitamin for the curation of a rachitic rat lies at a daily dose of 5/1000.000 mgr. during 10 days.

Natuurkundig Laboratorium Philips' Gloeilampen Fabrieken.

Chemistry. — *Coacervation (Partial miscibility in colloid systems).*
(Preliminary Communication). By H. G. BUNGENBERG DE JONG
and H. R. KRUYT.

(Communicated at the meeting of September 28, 1929).

Introduction.

For the last ten years we have been studying the nature of lyophilic colloids on the ground of the behaviour of sols. The experimental results at which not only we ourselves, but also others, have arrived, have led us to a definite conception about the state in which these systems are. This conception may be schematically expressed in these words: *polymolecular particles stabilized by solvation and capillary-electric charge.*

So far we have confined ourselves to stating that removal of the stabilizing factors leads to an annihilation of the colloid system, to a "flocculation", which in analogy to flocculation in hydrophobic colloids we represented for the sake of simplicity as a combining of the discharged and desolvated particles themselves. But earlier experiences of others as well as our own observation have taught us that we then described only the transition from an initial state (the sol) to a final state (solid precipitant with above liquid), though a very characteristic architectonic intermediate state exists, i.e. an "unmixing", a formation of drops, which may even manifest itself as a separation into two liquid layers.

These phenomena of unmixing have many times been the subject of an investigation, especially in systems in which two colloids are found, which each in itself can give stable sols in water, but which together give rise to phenomena of unmixing. In this connection we may mention the names of several compatriots: BEYERINCK, W. P. A. JONKER, TIEBACKX, REINDERS, but also of many others, of whom we only mention WO. OSTWALD¹⁾ and his collaborators, in whose treatises the earlier literature is also extensively discussed.

These "phenomena of unmixing" have a superficial resemblance to those in ternary systems; to give a better survey of the results the current triangle diagrams may be applied, but already in 1911 in a discussion at the 12th Physical and Medical Congress at Groningen one of us pointed out to what errors this analogy may give rise: for the visible separation of a (quasi homogeneous) sol into its components need, for instance, by no means be accompanied with a change of the number of phases.

The word "unmixing" having already a definite meaning, it seems desirable not to use the same word for the phenomenon in colloid systems

¹⁾ Koll. Z. **43**, 131 (1927); **47**, 258 and 357 (1929).

discussed here. Hence we introduce for this the word *coacervation*; the choice of this word will be discussed presently.

We wish to set forth in this paper how the phenomenon of coacervation fits into the system of our theory for lyophilic colloids. We will briefly mention also investigations which have not yet been published, and which have, indeed, not yet been entirely completed.

Experiments.

When one inquires into causes that call forth coacervation in a lyophilic sol, one is struck by the fact that these causes too bring about flocculation with sometimes very slight modifications of the circumstances, and even unmodified in the case of very analogous systems. Here follows a survey of a number of different procedures, in which (reversible) flocculation may be obtained, and with each procedure we will describe one or more cases, in which we can easily succeed in obtaining coacervation instead of typical flocculation. In what follows we denote by the terms macro- resp. micro-coacervation whether the coacervate forms a coherent liquid layer or is divided in microscopically visible drops.

1. *Flocculation with aliphatic alcohols.* The isostable proteins flocculate at the iso-electric point, when a sufficient quantity of alcohol is added. At 40—50° alcohol very easily brings about micro- and, after standing for a short time, macro-coacervation in an iso-electric gelatin sol.

2. *Flocculation with aliphatic alcohols + little electrolyte.* If to a 1 % gum arabic sol containing 50 m. eq. KCl, alcohol is added till the moment that just a permanent precipitate is formed, after which the substance is boiled up for a moment, one obtains, instead of floccules which are not to be differentiated microscopically, a beautiful coacervated system.

3. *Flocculation with a (poly-) phenol (crystalline tanning materials and tannin included).* In the immediate neighbourhood of the iso-electric point the simple phenols (phenol, pyrocatechin, resorcin, hydroquinone, pyrogallol, oxyhydroquinone, phloroglucine) flocculate isostable proteins. With all the above mentioned phenols ¹⁾ micro- and macro-coacervation with an iso-electric gelatin sol is easily obtained at 40°. One of the factors favourable to micro-coacervation, i.e. the slow action of the flocculating agent, can be realised here by means of slow cooling, as the phenols are not active, or at least much less active at higher temperature. On slow cooling homogeneous liquid drops are formed. They become less and less aqueous, but remain homogeneous. Fig. I shows such drops, which have been formed by the cooling to 42° of a 1.3 % iso-electric gelatin solution, in which 33 % resorcin. The drops are homogeneous at 40°, but in consequence of the relatively rapid cooling during the photographing a

¹⁾ H. G. BUNGENBERG DE JONG, Rec. trav. chim. 48, 494 (1929).

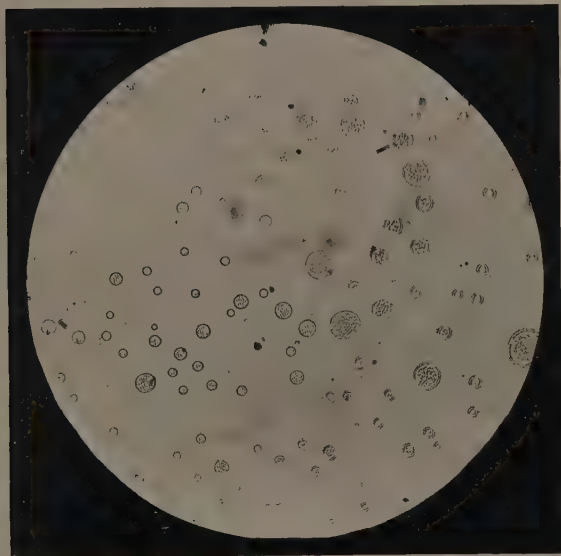


Fig. I. Gelatin + Resorcin; 65×

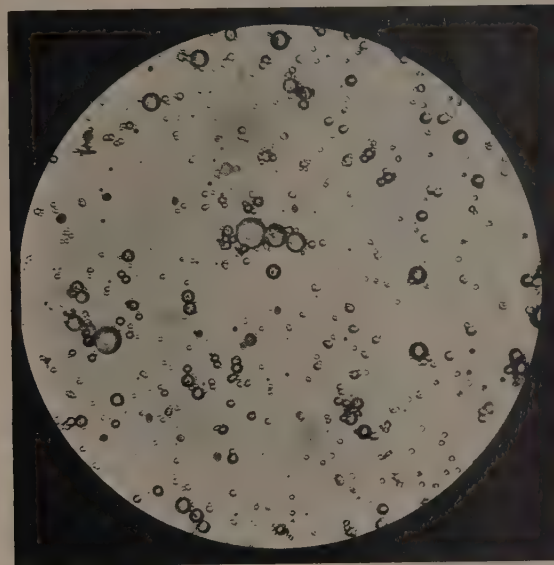


Fig. III. Gelatin + Tannin; 270×

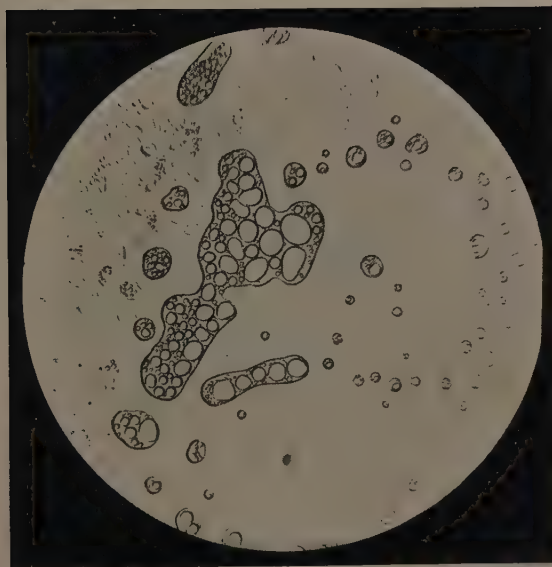


Fig. II. Gelatin + Resorcin; 110×



Fig. IV. Gelatin + Tannin; 270×

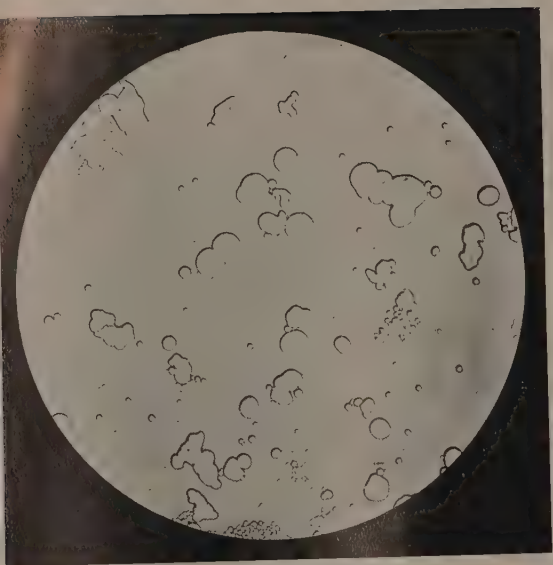


Fig. V. Casein; 220X

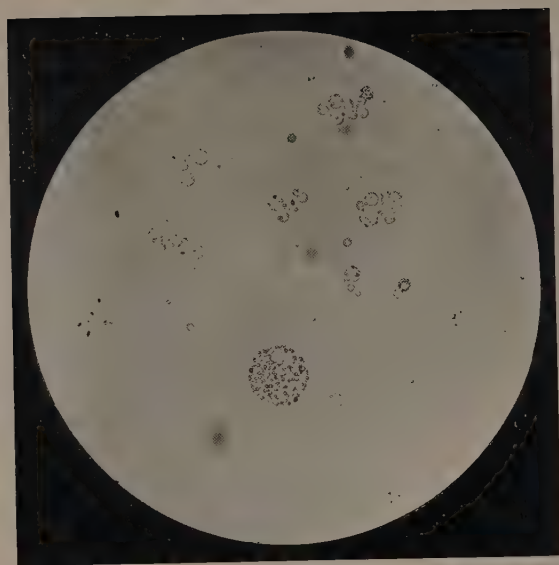


Fig. VII. Gelatin + $K_4Fe(CN)_6$; 310X

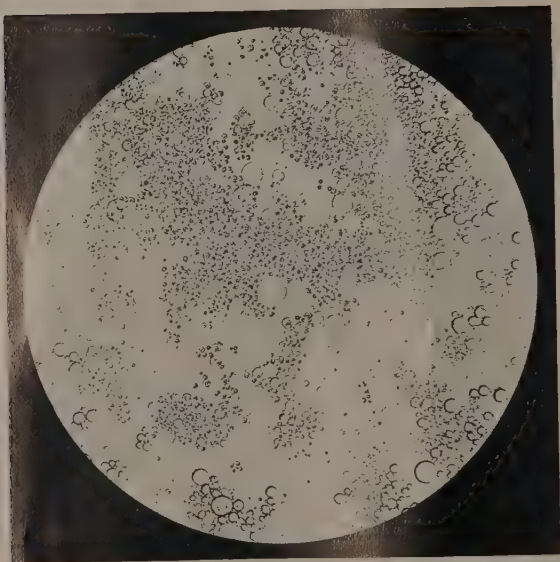


Fig. VI. Amandin; 245X

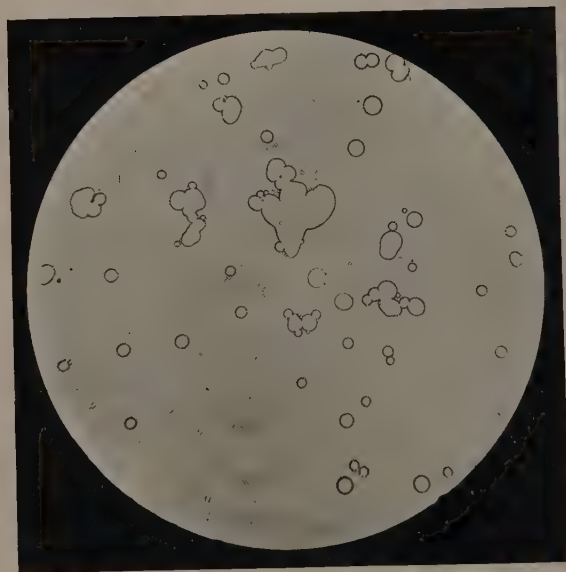


Fig. VIII. Serum Albumen + Gum Arabic; 120X

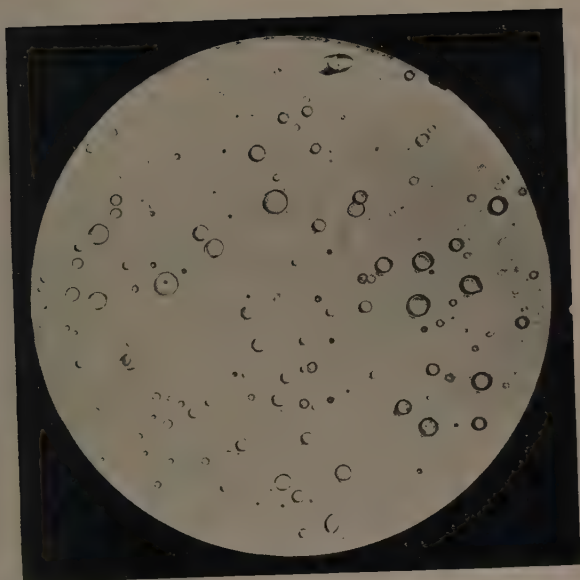


Fig. IX. Zeiss; 340X

vacuolisation has taken place. The same preparation was now rapidly heated and rapidly cooled, and then photographed (fig. II).

Just as with the simpler phenols, we also obtained coacervation in iso-electric gelatin with the following "crystalline tanning materials": d. catechin, chebulinic acid and Digalloyl glucose and further also with tannin. Fig. III shows a microphoto of this last combination, the same preparation showing a beginning of drops melting together, after it had stood for four hours at room temperature (fig. IV), a proof that at this temperature we have still to do with a liquid, though with an exceedingly viscous one.

4. *Flocculation with a (poly) phenol + little electrolyte.* Well purified agar does not flocculate with well purified tannin, a little electrolyte added brings about flocculation at once. On application of high temperature and slow cooling the micro-coacervation of the agar sol with this tannin solution succeeds easily.

5. *The salting out.* At higher temperature the micro-coacervation of the gelatin sol succeeds very easily with the following salts: Na_2SO_4 ¹⁾, $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 , ZnSO_4 , HgCl_2 , Na-tartrate, Na-citrate, Na-lactate, Na-succinate, Na-formiate, NaNO_3 , KNO_3 , NaNO_2 , MnSO_4 , FeSO_4 , NiSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, K_2CO_3 , NaCl, KCl, NH_4Cl . To this category belong probably also the salting out phenomena, which may be observed in not too greatly diluted soap solutions, as sodium oleate with NaCl or K_2CO_3 ; the "coagulate" may then also appear in the form of drops.

6. *Flocculation of iso-unstable proteins at the iso-electric point.* Addition of diluted NaOH to a caseinsol peptized in diluted HCl to near the iso-electric point brings about typical micro-coacervation at higher temperature (fig. V).

7. *Flocculation of hydrophile sols with small electrolyte concentrations.* The iso-unstable proteins are flocculated from their sols by some electrolytes in small concentrations. At 50° we obtained micro-coacervation in an alkalic casein sol by addition of a small quantity of CaCl_2 , SrCl_2 or BaCl_2 . To this category belongs also the flocculation shown by a number of carbohydrate sols (gum arabic, Carrageen- and Semen Lini mucilage) with small concentrations of electrolytes with multivalent kations. It is easy to convince oneself that hexol salt brings about micro-coacervation of the gum arabic already at ordinary temperature.

8. *Flocculation of the globulins after removal of the neutral salt.* Already OSBORNE and STRAUSS ²⁾ observed that in dialysis of an

¹⁾ WO. OSTWALD. Kleines Praktikum der Kolloidchemie, TH. STEINKOPFF. Dresden und Leipzig, 1922 p. 147.

²⁾ TH. B. OSBORNE and E. STRAUSS in Handbuch der biolog. Arbeitsmethoden herausgeg. von E. ABDERHALDEN, Abt. I Teil 8, p. 413 (1922).

amandine sol in NaCl solution this globulin separates out in the form of small globules. We have followed OSBORNE and STRAUSS's prescription to the first dialysis (inclusive), and made the micro-photograph reproduced in fig. VI of the "precipitated" globulin obtained.

9. *Temperature influence in protamin sols.* KOSSEL¹⁾ describes that at higher temperature a "clupein sulphate"-solution is clear, but that on cooling part of it separates from it as an "oil". Similar indications for coacervation in consequence of decrease of temperature are also found for other protamins, e.g. salmin.

10. *Flocculation of proteins with some special reagents.* WO. OSTWALD (l.c.) already published an extensive investigation of the macro-coacervation of gelatin sols with sulfo-salicylic acid.

Micro-coacervation of the gelatine sol succeeded further with picric acid (by slow cooling of the sol mixture which was clear at higher temperature), with $K_4Fe(CN)_6$ + a little HCl (fig. VII), and finally with trichlor acetic acid.

11. *Mutual flocculation of a positively and a negatively charged hydrophile colloid.* The typical example of this flocculation is the combination gelatin + gum arabic + a trace of acid, first described by TIEBACKX²⁾, and later studied by REINDERS³⁾, who observed that at somewhat higher temperature macro-coacervation easily sets in. We found micro-coacervation with the combination of gelatin with four vegetable mucilages: Carrhagean, Semen Lini, Cetraria Islandica, Semen Psyllii. A very beautiful coacervation was presented by the combination gelatin + "Na-nucleinate".

Instead of gelatin also another protein may be taken, e.g. serum albumin, egg albumin or an aqueous extract of "Ichtyocolla". The condition for the appearance of flocculation, resp. micro- or macro-unmixing is always that the P_H is such that one component the (protein) is positively charged, and the other component has not yet lost too much of its negative charge⁴⁾.

A micro-photograph for the combination gum arabic + serum albumin (prepared according to the THE SVEDBERG method⁵⁾) is represented in fig. VIII. To this (for biology highly important) group we can probably take also the flocculation of "basic" albumens with serum albumin gelatin, Na-nucleinate, etc.

12. *Flocculation of the prolamines-sols by water.* In contrast with other proteins the prolamines are peptized well by strong alcohol solutions, while

1) A. KOSSEL, Z. f. physiol. Chemie **22**, 178 (1896).

2) TIEBACKX. Kolloid Z. **8** (1911); **9** (1911); **31** (1922).

3) REINDERS. Chem. Weekblad **10** (1913).

4) H. G. BUNGENBERG DE JONG en W. A. L. DEKKER. Bioch. Z. **212**, 318 (1929).

5) THE SVEDBERG and BERTIT SJÖGREN. J. Am. Chem. Soc. **50**, 3318 (1928).

they flocculate on dilution with water. According to OSBORNE and STRAUSS's prescription ¹⁾ we prepared zein and slowly added water to a 1 % sol in 70 % alcohol at 40°, till a slight turbidity arose. After the substance had been left for some time at 40°, it was slowly cooled down to room temperature. Then a micro-photograph was made (fig. IX), which again beautifully reveals micro-coacervation.

Theoretical Considerations.

Coacervation and flocculation are, accordingly, very closely allied phenomena, both require elimination of the stability factors, charge and hydration. This can, of course, best be verified by studying how the relative viscosity of the system changes, when gradually the conditions are created that lead to coacervation. We have actually examined this in all the cases we have just described, and we shall soon publish the results in the "Koll. Zeitschr.". In these investigations we have indirectly succeeded in ascertaining that an amicro- resp. ultramicro-coacervation frequently precedes the perceptible coacervation.

Hence we have found that removal (resp. great decrease) of charge and hydration are conditions both for the coacervation and the flocculation; under these circumstances partial or entire separation of dispersion medium and dispersed phase sets, therefore, in; in flocculation the dispersed phase presents itself as solid aggregate, in coacervation as a viscid but yet "tropfbare Flüssigkeit", a liquid, which must therefore contain the solid particles, but also liquid (i.e. water in a hydrophilic colloid). Accordingly water in the coacervate is in a condition in which it is not miscible with the large mass of the other water.

What image must we form to ourselves of the structure of the coacervate, so that this image is in harmony with that for the state of sol and flocculation? The image must account for the fact that the particles in the sol continue in permanent division in their surroundings, also e.g. when water is added, but that in the coacervate they remain bound to the smaller quantity of water in the coacervate. Besides their condition must be thought so, that reversibly the sol-condition can be restored, as soon as charge and (or) hydration are restored. These considerations at once suggest the following image: in the coacervated phase are the particles with a limited quantity of water of hydration ²⁾, but they maintain themselves as primary particles; this limited quantity of water must, therefore, necessarily be somewhat differently bound than the water of hydration in the sol-condition.

Two things are to be considered here: first the name. As we saw the coacervate is a drop or a layer, in which the particles have flocked together as bees in a swarm. Unfortunately it is hardly possible to form a word from

¹⁾ TH. B. OSBORNE and E. STRAUSS, loc. cit. p. 443.

²⁾ For the sake of simplicity we confine ourselves for the moment to water: one may of course, read every time equally well solvation — and intermicellar liquid.

the Latin word: *examen* that does not lead to comical associations; the Greek word *smenos* is unsuitable, and the German word *Schwarmbildung* has already been taken possession of in the theory of the mesomorphous phases. We, therefore, chose the Latin *acervus* = aggregation, heap, and wish to express the previous combining in the prefix *co*.

In the second place we should try to make it clear to ourselves what these two kinds of water bonds are; in this we may make use both of classical conceptions of VAN BEMMELEN and of modern analogies in the theory of the electrical double layer (GOUY).

For certain reasons the solvation of the lyophilic colloids suggests the word "solvation mantle" to the investigator. Not that it would a priori be certain that all the water, like a mantle, would quite envelop a solid nucleus; on the contrary, it is possible to advance objections to such a rigid image. But part of the water *must* surround the particle like a mantle, if we wish in any way to account for the fact that the solvation acts as a stabilizing factor; for on discharge of lyophilic colloid particles it often prevents the coalescence, which might be expected on the ground of the free surface energy. Hence the solvation must change something in this surface, and this so, that this free surface energy does not manifest itself. It is for this reason that the conception according to which the hydration mantle would surround the particle as a sharply defined phase, does not satisfy us; for in a collision these sharply defined mantles would come in contact, and it is not easy to see why they should not unite.

We should be more inclined to suppose the original surface energy between particle and dispersion medium to be practically annihilated by the solvation. A concrete boundary can, therefore, not exist; we must rather assume with VAN BEMMELEN¹⁾ that the solvation consists of liquid bound more and more loosely towards the outside, and finally passes imperceptibly into the perfectly free liquid of the dispersion medium. A real boundary can scarcely be indicated, we, therefore, propose to denote such a solvate mantle by the term of *diffuse solvation mantle*.

When, therefore, by the aid of EINSTEIN's formula we calculate from the viscosity of a sol, how many cc. of solvate liquid are bound by 1 gr. of colloid substance, we obtain a number that is of course quantitatively wrong, for the application of EINSTEIN's formula assumes a rigid particle, i.e. in our case, therefore, a particle with rigid solvate mantle with a concrete limitation with regard to the dispersion medium.

Rigid is, in our opinion, possibly only the very first molecule layer round the particle, but the further we get towards the outside, the greater becomes the mobility of the solvate molecules, so that finally the solvate mantle imperceptibly passes into the free dispersion medium. We can now readily see that the preparative process that eventually renders possible the combination of the particles to a coacervate, can only consist of the transition of

¹⁾ J. M. VAN BEMMELEN, Z. anorgan. Chem. 13, 234 (1896).

the diffuse solvate mantle into a solvate mantle with a concrete boundary at its periphery. We shall denote such a solvate mantle by the term of *concrete solvation mantle*. To make the matter clearer we may point out that such a condition of the solvate mantle differs from a diffuse solvation mantle only at its periphery. In its inner layers we still suppose it to consist of concentric shells of decreasing degree of binding, i.e. increasing mobility of the solvate molecules, hence still far from rigid.

The mechanism of the process is in outline represented in fig. X. Symbol A represents a particle with a diffuse solvate mantle (dotted periphery).

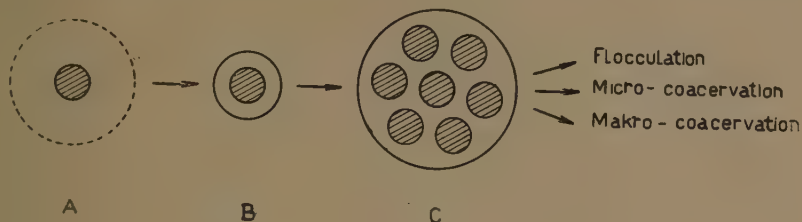


Fig. X.

According as desolvation sets in, we must assume that at the same time with the shrinking of the solvate mantle, this becomes more and more concrete at its periphery. Let symbol B now represent such a particle, in which, to indicate the concrete boundary, we have no longer dotted, but traced the periphery of the solvate mantle. In the case of sufficient free surface energy of the mantle boundaries such particles can now combine to a coacervate with their solvate mantles.

According as the process of combining has advanced in a given time, we get typical flocculation, micro- or macro-coacervation.

We see accordingly that according to our view the original particles in the coacervation process have only combined with their solvation mantles. This accounts for the fact that coacervations have the nature of a liquid, because the solvate liquid should not be considered as rigid, but consists of liquid which in a more or less degree has lost its free mobility. We have seen that the most obvious preparation for the coacervation process is desolvation. It can be brought about by change of the material constitution of the dispersion medium (categories 1, 2, 3, 4, 5, 8, 10, 12).

In other cases it can be brought about by decrease of charge (categories 6, 7). It is not at all strange that also in the latter case a diffuse solvate mantle could pass into a concrete one, considering the well known influence of charge on the surface tension. It is not quite so easy to see that if two opposite charges are balanced, the mantles can also become concrete (category 11).

So we see that the finer mechanism through which a diffuse mantle can pass into a concrete one, can be very different, and it will be reserved for

later researches, to study this mechanism more thoroughly. The conception of the nature of the coacervation process set forth here, now enables us to study the properties of the solvate liquid more closely also experimentally. For the equilibria between the originally free particles and the dispersion medium have their continuation in the equilibria between the coacervate and the equilibrium liquid.

Both liquid layers are now accessible to chemical analysis (i.e. material constitution) as well as to physicochemical investigation. Researches in this direction have already been started.

Dr. H. L. BUNGENBERG DE JONG and Miss W. KLAAR have, as we heard from them, studied analogous phenomena simultaneously with us but quite independently. They investigated especially the gliadin sol and came to conclusions similar to ours.

Biological Significance of the Coacervates.

When we pose the question whether the coacervates have biological significance, we must for the present observe all possible reservation.

On closer inspection of the ground mass of the protoplasm, it strikes one that this has some properties in common with the coacervates, so that there is a possibility that this ground mass may be considered as a coacervate or as a system of coacervates. For the protoplasm is often considered as an isotropic, liquid, concentrated colloid water system limiting itself¹⁾, and often presenting a tendency to vacuolisation²⁾ (compare fig. II).

Coacervate drops further exhibit a tendency to absorb solid particles e.g. carbon and indigo carmine particles. They often assume a very intense colour with several pigments, (e.g. coacervate drops of gum arabic + gelatin, with lithium carmine, Eosine, Nigrosine, and they also strongly absorb Collargol).

Whether the points of resemblance summed up here are only a coincidence, we cannot yet decide.

It certainly seems justifiable to assume that for the structure of living matter, and also for its outer limitation, not only sols and structure elements (gels, fibrils etc.) have significance, but that by the side of them, likewise coacervates play a part.

¹⁾ W. LEPESCHKIN, *Kolloidchemie des Protoplasmas*, JULIUS SPRINGER, Berlin. 1924, p. 142.

²⁾ L. V. HEILBRUNN, *The Colloid Chemistry of Protoplasma*, Gebr. BORNTAEGER, Berlin 1928, p. 233—255.

Chemistry. — *Die ungleichmäßige Verteilung der stabilisierenden Faktoren über die Oberfläche kolloider Teilchen.* Von H. R. KRUYT.

(Communicated at the meeting of September 28, 1929).

In einer kürzlich erschienenen Abhandlung hat BUNGENBERG DE JONG ¹⁾ darauf hingewiesen, dass die Gelatinierung und das Verhalten der Gele sehr gut verständlich wird, wenn man annimmt, dass die schützenden Faktoren, Ladung und Hydratation, nicht gleichmäßig über die Oberfläche der Teilchen verteilt sind, sondern stellenweise auf dieser vorkommen. Dieser Gedankengang scheint mir eine nach allen Seiten glückliche Lösung zu bedeuten, da derselbe bisher unerklärbare Tatsachen plötzlich begreiflich macht. Es besteht jedoch Grund, nunmehr noch einen Schritt weiter zu gehen und diese Betrachtungsweise nicht auf lyophile Kolloide zu beschränken, sondern sie allgemein für kolloide Teilchen und somit auch für lyophobe Teilchen als anwendbar zu erachten. Bei diesen handelt es sich allein um die elektrische Ladung als Stabilitätsfaktor.

Das Bild, welches man sich bisher von einem Kolloidteilchen machte, ist

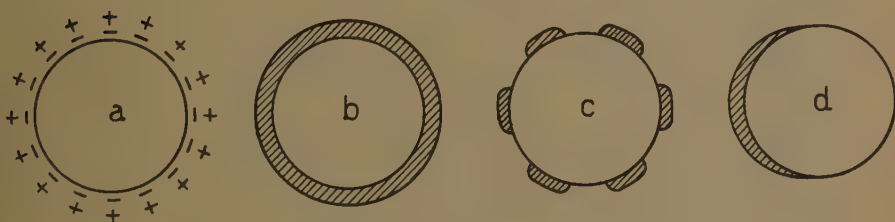


Fig 1

in Abb. 1 a skizzenartig wiedergegeben. Einfachheitshalber ist eine Doppelschicht nach HELMHOLTZ und nicht eine diffuse Schicht nach GOUY gezeichnet. In Abb. 1 b ist dieselbe Sachlage, doch etwas mehr schematisch in Bild gebracht. Der hellere Teil soll immer das Teilchen darstellen und die dunklere Zone die elektrische Doppelschicht oder wenigstens die Wirkungssphäre der elektrischen Abstosung. In Abb. c ist nun weiter die Annahme zum Ausdruck gebracht, dass diese Abstosungssphäre nicht homogen über die Oberfläche verteilt, sondern lokalisiert ist. Abb. d gibt dasselbe wieder; aber noch schematischer, indem angenommen wird, dass die Oberfläche des Teilchens zur Hälfte geladen und zur andern Hälfte

¹⁾ H. G. BUNGENBERG DE JONG: Z. physik. Chem. **130**, 205, 1927.

ungeladen ist. Es ist selbstredend, dass ein Sol mit derart konstituierten Teilchen kataphoretische Bewegung aufweisen wird, ebenso wie ein Sol vom Typus *b*. Die Bewegung wird jedoch in den Fällen *c* bzw. *d* geringer sein als im Falle *b*, wenn übrigens die elektrische Ladung per Flächeneinheit in der geladenen Aera dieselbe ist; wird doch die gewöhnliche Gleichung

$$He = \eta \frac{du}{dx}$$

(in welcher *H* den angebrachten Potentialunterschied,
e die Ladung der Oberfläche per qcm,
 η den Reibungskoeffizienten,
 $\frac{du}{dx}$ das Geschwindigkeitsgefälle darstellt),

die per qcm Oberfläche gilt, nunmehr:

$$\Sigma He = \Sigma \eta \frac{du}{dx}$$

jedesmal über die Oberfläche summiert, wo Ladung, bzw. wo Reibung ist. Wenn wir nun annehmen, dass die Hälfte der Oberfläche mit einer Doppelschicht besetzt ist, dann wird sich die Gleichung folgendermassen gestalten:

$$\frac{1}{2} He = \eta \frac{du}{dx} \quad \text{und } ^1) \quad \zeta = \frac{12\pi}{HD} u$$

Darf also bezüglich $\frac{du}{dx}$ angenommen werden, dass diese Grösze in dem Falle *b* und *c* oder *d* denselben Wert hat, dann wird die kataphoretische Geschwindigkeit im Falle *c* oder *d* dieselbe sein wie in *b*, wenn das Potential in dem ersteren Falle doppelt so gross ist wie in dem zweiten Fall. Die Stabilität des Sols wird nun jedoch durchaus nicht der kataphoretischen Geschwindigkeit proportional sein. Die Haftwahrscheinlichkeit wird, auch wenn ζ in den schützenden Teilen oberhalb des kritischen Wertes ist, im Falle von 50 % Bedeckung 0.25 sein; sind doch 50 % der Oberfläche ungeschützt und werden Kollisionen zweier ungeschützter Streifen Verklebung der Teilchen bewirken. Die Wahrscheinlichkeit einer solchen effektiven Kollision ist $0.50 \times 0.50 = 0.25$.

Die Vermutung, dass Sole vom Typus *c* oder *d* vorkommen, ist namentlich in denjenigen Fällen berechtigt, in denen eine vorangehende teilweise Entladung gerade stattgefunden hat. Auch wenn ein gegebenes Sol entsprechend dem Typus *b* konstituiert ist, bleibt noch die Vermutung annehmbar, dass Entladung nicht immer homogen über die ganze Oberfläche stattfindet, sondern dass wenigstens anfangs der Typus *c* oder *d* auftreten wird. Wenn nämlich die Oberfläche nicht gut leitet (worüber

¹⁾ Entsprechend der DEBYE'schen Formel, Physik. Z. 25, 49, 1924.

gleich ein Näheres), würde es vielmehr wundernehmen, wenn die Entladung völlig uniform über die Oberfläche erfolgte.

Wenn wir nun den Fall näher betrachten, dass sich ein Doppelteilchen gebildet hat, bei dem jedes der Bestandteile zur Hälfte seiner Oberfläche durch eine elektrische Ladung geschützt ist (also zwei Teilchen vom Typus *d*), dann lässt sich ein solches Teilchen schematisch darstellen wie in Abb. 2.

Soll nun verfolgt werden, wie gross die Haftwahrscheinlichkeit solcher Doppelteilchen ist, dann ergibt sich auch hierfür laut Schätzung für die Haftwahrscheinlichkeit $\frac{1}{4}$, da ja zwei Halbkugeln vorliegen, die geschützt sind, also $2 \times 2\pi r^2$, und eine ungeschützte Zylinderoberfläche in Grösze von $2\pi r \times 2r$. Man sieht also, dass die Haftwahrscheinlichkeit des Doppelteilchens gleich $0.5 \times 0.5 = 0.25$, also gleich derjenigen des Einzelteilchens ist.



Fig 2

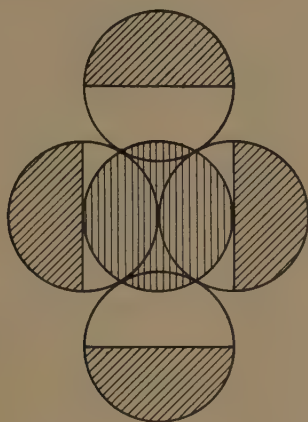


Fig 3

Ganz anders werden die Verhältnisse aber, wenn mehrere Teilchen zusammentreten. Legen sich dem Doppelteilchen noch zwei Teilchen an, wie in Abb. 3 wiedergegeben ist (unter Weglassung des mittleren Kreises, worauf gleich zurückgekommen werden soll), dann lehrt eine annähernde Berechnung, dass das Verhältnis zwischen geschützter und ungeschützter Oberfläche gleich 2 : 1 und dass somit die Haftwahrscheinlichkeit eines vierfachen Teilchens 0.11 ist. Nimmt man an, dass sich einem solchen vierfachen Teilchen noch zwei weitere anlegen, wie dies in Abb. 3 durch die Hineinzeichnung des mittleren Kreises zum Ausdruck gebracht ist, dann lehrt eine ähnliche Berechnung, dass das Verhältnis des geschützten und des ungeschützten Teiles der Oberfläche sich etwa wie 1 : 2 verhält und dass infolgedessen die Haftwahrscheinlichkeit 0.06 beträgt.

Aus den letzteren Ziffern erhellt aufs deutlichste, dass bei stellenweiser Entladung die Haftwahrscheinlichkeit des Konglomerates bei fortschreitender Koagulierung immer geringer wird.

Zwar wurde ein sehr einfacher Fall zur Basis unserer Betrachtung genommen, nämlich der Fall, dass die ganze Ladung auf die eine Hälfte des Teilchens konzentriert ist; aber es ist klar, dass im allgemeinen die Haftwahrscheinlichkeit in demselben Masse abnimmt wie die teilweise entladenen Teilchen zusammentreten, da sie immer die geladenen Zonen nach auszen wenden werden. Diese Tatsache nun vermag einen Einblick in verschiedenen Probleme der Kolloidchemie zu verschaffen. Um dies zu erläutern, wird im Nachstehenden fortgesetzt das schematische Beispiel herangezogen werden, in welchem die Ladung auf eine Halbkugel konzentriert gedacht wird.

Die Kinetik der Koagulation.

VON SMOLUCHOWSKI hat in seinen klassischen Abhandlungen über Koagulation¹⁾ eine Theorie über die sog. schnelle Koagulation entwickelt, d.h. für den Fall, dass jede Kollision eine Verklebung mit sich bringt, wobei also die Haftwahrscheinlichkeit gleich 1 ist. Er gelangt zu dem Schluss, dass die Anzahl Teilchen n mit der Zeit sich derart ändert, dass

$$n = \frac{n_0}{1 + \frac{t}{T}} \quad \text{oder} \quad T = \frac{nt}{n_0 - n}$$

in welcher Formel n_0 die ursprüngliche Teilchenanzahl und T die sog. Koagulationszeit (Halbierungszeit) bedeutet.

Verschiedene Untersuchungen haben bewiesen, dass Messungen von n zu verschiedenen Zeiten in der Tat einen konstanten Wert für T ergeben.

VON SMOLUCHOWSKI meinte, dass bei langsamer Koagulierung diese Formel den Verlauf ebensogut wiedergab, aber dass nur die Konstante T mit einer Grösze ε multipliziert werden musz, welche letztere durch den Prozentsatz der Kollisionen mit wirklichem Verklebungseffekt, also durch die Haftwahrscheinlichkeit, bestimmt wird.

KRUYT und VAN ARKEL²⁾ fanden jedoch, dass im Fall der langsamen Koagulation bei Selenolen T , bzw εT , keineswegs eine Konstante ist, und andere Forscher haben seitdem diese Ergebnisse für andere Sole bestätigt. Aus den von uns angestellten Untersuchungen mit dem Selenol zeigte sich aufs deutlichste, dass die Halbierungszeit T mit der Zeit steigt.

Der im vorigen Abschnitt dargelegte Gedankengang scheint nun dieses unerwartete Verhalten erklären zu können. Die Haftwahrscheinlichkeit ist

¹⁾ M. VON SMOLUCHOWSKY, Z. physik. Chem. 92, 129 (1918). Auch Physik. Z. 17, 557 und 583, 1916.

²⁾ H. R. KRUYT und A. E. VAN ARKEL: Rec. Trav. Chim. 39, 656 (1920); 40, 169, (1921); Koll. Z. 32, 29 (1923).

während des Koagulationsprozesses in der Tat nicht konstant, sondern sie wird durch das Aneinanderlegen der örtlich entladenen Teilchen allmählich geringer und die berechnete Halbierungszeit musz daher allmählich grösser werden.

Auch andere Einzelheiten der Untersuchung über die Kinetik der Selensole lassen sich in diesem Lichte gut erklären. Es war uns seinerzeit schon aufgefallen, dasz die *sehr* langsame Flockung sich dem normalen Verlaufe nach VON SMOLUCHOWSKI viel mehr näherte als die mittelmässig langsame Flockung. Diese nimmt also eine stark abweichende Zwischenstellung zwischen der schnellen und der sehr langsamen Koagulation ein, die einen gleichen Typus aufweisen. Dies ist nun sehr gut begreiflich: Im Falle der schnellen Koagulation ist die Ladung sogut wie ganz weggenommen; die Haftwahrscheinlichkeit ist 1 und sie bleibt 1 während des ganzen Koagulationsprozesses, weil keine Restladungen vorhanden sind. Sehr langsame Flockung findet dagegen statt, wenn die ursprüngliche Ladung nur wenig herabgesetzt ist: Die Teilchen zeigen den Typus 1 b mit verkleinerter Sphäre, oder Typus 1 c, mit noch sehr vielfachen Ladungszonen; in beiden Fällen ändert sich die Haftwahrscheinlichkeit nicht oder wenig bei Vergrößerung der Teilchen. Schnelle und sehr langsame Flockung werden also nach der Gleichung VON SMOLUCHOWSKI's erfolgen, mittelschnelle jedoch nicht, gerade wie VAN ARKEL und ich dies fanden.

Reversible Flockung und Peptisierung.

Wenn man die elektrische Ladung als gleichmässig über die Oberfläche eines kolloiden Teilchens verbreitet betrachtet, wird es sehr schwer zu begreifen, wie es möglich ist, ein einmal verklebtes Teilchenpaar durch Aufladung wieder zu trennen. In Zusammenhang hiermit ist es auch schwierig, den Unterschied zwischen primären Teilchen und Polyonen zu formulieren. Denn ein Konglomerat völlig entladener oder gleichmässig sehr schwach geladener Teilchen braucht doch bei gleich verteilter Aufladung der Oberfläche dadurch keineswegs in Unterteile zu zerfallen. Ganz anders wird die Sachlage jedoch, wenn die Ladungen örtlich vorhanden sind.

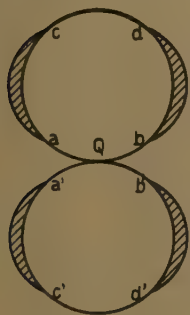


Fig. 4

Abb. 4 gibt wieder eine skizzenartige Darstellung zweier Teilchen, die zusammengetreten sind. Bei den primären Teilchen waren die Stücke *ab* und *cd*, bzw. *a'b'* und *c'd'* ungeschützt und die Stücke *ac* und *bd*, bzw. *a'c'* und *b'd'* geschützt. Es wird nun angenommen, dasz diese Teilchen in *Q* verklebt sind. Die Lage der abstosenden Stücke *ac* und *a'c'*, *bd* und *b'd'* bewirkt, dasz weitere Vereinigung durch die Abstosung der genannten Gebiete untereinander behindert wird.

Wenn man bei einem geflockten Kolloid, wie dem Sol von V_2O_5 den

entladenden Elektrolyten durch Auswaschen¹⁾ entfernt, oder wenn man präzipitiertem HgS oder SnO_2 einen geeigneten aufladenden Elektrolyten hinzusetzt, so bewirkt man offenbar eine Ausbreitung der bereits vorhandenen Doppelschichtfragmente. Je mehr die geladenen Gebiete ac , $a'c'$, bd oder $b'd'$ sich in der Richtung nach Q ausdehnen, um so grösser wird in entsprechendem Grade die Abstossung der Teilchen untereinander. Die zunehmende elektrische Ladung wirkt somit als ein Keil in der Oeffnung aQa' und bQb' und spaltet demzufolge das Aggregat auf.

Natürlich ist für einen solchen Peptisationseffekt erforderlich, dass die primären Teilchen hinreichend erhalten geblieben sind, dass also weder die Koagulation allzu effektiv gewesen ist, noch dieser Aggregationszustand zu lange gedauert hat. Die Untersuchung hat nämlich gelehrt, dass Koagulation des V_2O_5 -Sols durch Barium- oder Aluminiumsalze mit ihren steil verlaufenden ζ - c -Kurven eine irreversible Flockung bewirkt, offenbar ist dort die Doppelschicht völlig weggenommen und der Mechanismus der oben beschriebenen Repeptisation daher unmöglich. Flockt man dagegen mit Alkalimetallkationen, welche sehr allmählich entladen (flach verlaufende ζ - c -Kurve), dann ist die Aussicht auf stellenweise Entladung naturgemäss viel grösser; in der Tat erwies sich unter jenen Umständen das Koagulat als repeptisierbar. Des weitern zeigte sich, dass man die Koagulate nicht mehr peptisieren kann, wenn sie langem Stehen ausgesetzt gewesen sind; es wird dadurch eine weitgehende Verklebung („Einformung“ in Q) stattgefunden haben; auch wird dadurch die Möglichkeit geschaffen, dass die übriggebliebenen Ladungszonen sich gleichmässiger ausgebreitet haben.

Die Frage, ob sich primäre Teilchen zu Polyonen vereinigt haben, wird daher von der Frage beherrscht, wie die Balance der anziehenden Kräfte in Q gegenüber der grössten elektro-kapillaren Abstossung bei Qb und Qb' ist.

Was hier für die Ladung gesagt wurde, gilt natürlich ebenso sehr für die Hydratation, wenn diese in grösserem oder geringerem Masse als Stabilitätsfaktor auftritt. Wenn ac und bd , bzw. $a'c'$ und $b'd'$ Hydratationsgebiete sind, wird Ausdehnung jener Gebiete in der Richtung von Q ebenso gut ein Auseinanderweichen der Teilchen mit sich bringen. In vielen Fällen werden beide Faktoren zusammenwirken.

Andere Probleme.

Es erhebt sich nun sofort die Frage, ob die Oberfläche eines kolloiden Teilchens nicht eine Aequipotentialoberfläche sein muss. Falls die Oberfläche des Teilchens Elektrizitätsleiter wäre, ist es selbstredend, dass diese Oberfläche überall dasselbe Potential haben müsste; meine Annahme der nicht gleichen Verteilung der Ladung trifft also auf keine Schwierigkeiten, z.B. für ein Selenteilchen; man könnte jedoch meinen, dass sie sich nicht in bezug auf ein Goldteilchen aufrechterhalten lasse. Indessen ist m.E. ein

¹⁾ H. FREUNDLICH und W. LEONHARDT, Koll. Beitr. 7, 172 (1915).

elektrisches Leitungsvermögen der Auszenseite eines Goldteilchens keineswegs sicher, ist doch die Auszenschicht jenes Teilchens, d.h. die Doppelschicht und die unmittelbar an diese grenzende Schicht nicht aus metallischem Gold aufgebaut. PAULI und FUCHS¹⁾ wiesen nach, dass die elektrische Doppelschicht ringsum ein Goldteilchen aus den Ionen von Auratsalzen besteht, und die Untersuchungen VAN DER WILLIGEN's²⁾ haben es höchst wahrscheinlich gemacht, dass sich zwischen dem massiven Gold und dieser Aurat-Doppelschicht eine Goldoxydschicht befinden muss. Hiermit tritt die Möglichkeit in den Vordergrund, dass die Oberfläche des Teilchens nicht notwendigerweise eine Äquipotentialoberfläche sein muss; metallische Leitung ist sicherlich nicht vorhanden.

Diese Oxydhäute kommen wahrscheinlich vielfach vor; wirkliche Isolatoren für die Elektrizität werden sie andererseits jedoch vermutlich nicht sein. Dadurch wird auf die Dauer Ausgleich örtlicher Ladungen stattfinden können. Man muss hierin wahrscheinlich die Ursache der sog. „Alterungs- bzw. Gewöhnungserscheinungen“ erblicken, die so häufig bei kolloiden Lösungen beobachtet sind. Man denke z.B. an die Tatsache, dass das Erreichen des Flockungspunktes sehr von dem Umstande abhängig ist, ob man den flockenden Elektrolyten auf einmal oder in Portionen hinzufügt.

Der in Abb. 1 c und d dargestellte Zustand ist also ein vorübergehender; aber er ist bei der Flockung mit einer Elektrolytmenge ungefähr vom Grenzwert als eine metastabile Umwandlungsstufe zu betrachten, die sehr oft durchlaufen wird und sich eine Zeitlang hält. Die Verteilung der geladenen Stellen wird durch zufällige Besonderheiten bei der Mischung von Elektrolyt und Sol beherrscht, während auch die spezifischen Eigenschaften beider ihren Einfluss geltend machen werden.

Bisher hat man also den Flockungsprozess viel zu viel statisch aufgefasst. Man hat die elektrischen Erscheinungen eines flockenden Kolloids zuviel mit elektrischen Erscheinungen identifiziert, welche unter Umständen bestimmt wurden, bei denen sich Endgleichgewichte eingestellt hatten. Untersucht man z.B. den Einfluss von Elektrolyten auf Strömungspotentiale in Glaskapillaren, so wartet man gewöhnlich 24 Stunden, bevor man zur endgültigen Messung übergeht. Diese Wartezeit dient vermutlich gerade zum Ausgleich örtlicher Ladungsunterschiede.

Man bestimmt also auf diese Weise in der Tat das ζ -Potential, das dem Gleichgewicht nach zu der Elektrolytenkonzentration gehört; aber bei der Flockung vollzieht sich der Prozess, wenigstens zum Teile, ehe jenes Gleichgewicht in der Grenzschicht erreicht ist, und man muss somit bei der Erklärung dieses Prozesses sehr wohl der metastabilen Zwischenphase Rechnung tragen. Nur dann wird z.B. der Einfluss von Mischungsverhältnissen auf den Flockungsprozess begreiflich.

Utrecht, Augustus 1929.

VAN 'T HOFF-laboratorium.

¹⁾ W. PAULI und FUCHS, Koll. Beitr. 21, 412, 1925.

²⁾ P. C. VAN DER WILLIGEN, Diss. Utrecht, 1927, S. 122. u. f.

Physics. — *New measurements on the vapour pressure curve of liquid helium.* I. By W. H. KEESOM, SOPHUS WEBER and G. NØRGAARD.
(Communication N^o. 202*b* from the Physical Laboratory at Leiden.)

(Communicated at the meeting of September 28, 1929).

§ 1. *Introduction.* In Comm. N^o. 147*b* ¹⁾ the normal boiling point of helium could be fixed with sufficient accuracy and was found to be

$$T = 4.22^{\circ} \text{ K. } ^2).$$

At the lowest temperatures the pressure in the helium thermometer becomes very small, also because at those temperatures measurements must be done with a thermometer with low icepoint pressure. At those circumstances the thermomolecular pressure difference between thermometer bulb and manometer appeared to get very important. Therefore it is necessary, for obtaining an accurate determination of the vapour pressure curve down to the lowest temperatures, to take at hand an extensive research concerning the thermomolecular pressure differences in helium at the lowest temperatures.

A new research concerning the vapour pressure curve of liquid helium for the temperatures below the boiling point appeared necessary, also because the results of the measurements of Comm. N^o. 147*b* could but very insufficiently be expressed by a formula. The necessity of a new research became still more evident, when during the preparations for this research KEESOM and WOLFKE ³⁾ found, that the liquid helium undergoes a transformation at a vapour pressure of 38.65 mm. It hence follows that the vapour pressure curve of liquid helium consists of two parts, which cannot be represented by the same theoretical formula. In connection herewith it was very important to see if at the transformation temperature there is a measurable discontinuity in the slope of the vapour pressure curve.

At this research we could profit in a rather high degree by the

¹⁾ H. KAMERLINGH ONNES and SOPHUS WEBER. These Proceedings 18, 493, 1915; Comm. Leiden N^o. 147*b*.

²⁾ In Comm. N^o. 147*b* the correction for the thermomolecular pressure difference was calculated in two ways. One way gave for the boiling point of helium 4.22° K. , the other 4.21° K. This last number has been considered later as the most probable one, see e.g. Comm. Leiden Suppl. N^o. 60. On account of a new discussion of the experimental material of Comm. N^o. 147*b*, and considering what at present we know further about the correction concerning the thermomolecular pressure difference, we now prefer the number 4.22° K.

³⁾ W. H. KEESOM and M. WOLFKE. These Proceedings 31, 90, 1928 and 31, 800, 1928; Comm. Leiden N^o. 190*b* and 192*a*.

experiences acquired then. It had appeared not to be advantageous that the capillary of the helium gasthermometer consists of parts with different diameters ¹⁾, for this may cause a too great uncertainty in the corrections for the thermomolecular pressure difference, unless we measure accurately the temperatures at the soldering places. Also it had appeared desirable to determine more exactly the correction for the noxious volume. For this purpose we placed, in the way CHAPPUIS has indicated, an auxiliary capillary, that is a helium thermometer without bulb, alongside the helium thermometers.

Meanwhile the research, of which this Comm. gives an account, is limited to those temperatures, at which a separate extensive investigation on the thermomolecular pressure difference is not yet necessary.

§ 2. The thermometers. In determining the vapour pressure curve

of liquid helium the main point is the measurement of the temperatures. As has been done at the measurements of Comm. N^o. 147*b* we have used the gas thermometer with constant volume, filled with gaseous helium of a suitable pressure ²⁾.

We used two helium thermometers, Therm. I and III (Fig. 1), each one fitted with a hot wire manometer according to KNUDSEN ³⁾. Alongside them (see § 1) a thermometer without bulb (Therm. II) was placed, to eliminate the correction for the noxious volume.

The length of the small hot wire manometers was about 4 cm., the volume of each one about 0.6 cm³. As hot wire a Wollastonwire was used of about 7 μ diameter, with an electrical resistance of about 25 Ω per cm. at 0° C.

The capillaries of the thermometers were previously tested exactly. The calibration of the thermometers was performed by weighing with mercury or water. The constants of the thermometers were :

Thermometer N^o. I :

Volume of the bulb $A_1B_1 = 39.753 \text{ cm}^3./18^\circ \text{ C.}$

Diameter capillary $B_1C_1D_1E_1 = 0.2029 \text{ cm.}$

Volume $B_1C_1H_1D_1E_1 = 3.946 \text{ cm}^3./18^\circ \text{ C.}$

Volume hot wire manometer I $= 0.647 \text{ cm}^3./18^\circ \text{ C.}$

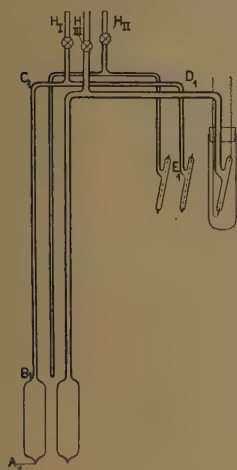


Fig. 1.

¹⁾ Comp. Comm. N^o. 147*b* § 3.

²⁾ For a discussion of the difficulties, which arise at the measurement of these very low temperatures, see Comm. N^o. 147*b*.

³⁾ M. KNUDSEN. Ann. d. Phys. (4) 35, 391, 1911 and (4) 83, 835, 1927. Comp. also Comm. Leiden Nos. 137*b* and c.

Thermometer N^o. II (without bulb) :

Diameter capillary $B_2C_2D_2E_2 = 0.2096$ cm.

Volume $B_2C_2H_2D_2E_2 = 3.115$ cm³./18° C.

Volume hot wire manometer II = 0.609 cm³./18° C.

Thermometer N^o. III :

Volume of the bulb $A_3B_3 = 40.319$ cm³./18° C.

Diameter capillary $B_3C_3D_3E_3 = 0.3694$ cm.

Volume $B_3C_3H_3D_3E_3 = 8.370$ cm³./18° C.

Volume hot wire manometer III = 0.626 cm³./18° C.

The hot wire manometers after having been mounted were surrounded with a glass tube filled with vaseline oil. The electrical resistance at 0° C. and the temperature coefficient of the resistance between 0° C. and 60° C. seemed fairly constant. For the Wollastonwire the temperature coefficient of the electrical resistance was $\alpha_{0-60} = 0.00282$.

During the calibration the hot wire manometers were immersed in a bath of finely planed ice and distilled water and connected with a system of pipettes according to KNUDSEN. The arrangement is represented in Fig. 2, whereas the electrical connections were quite analogous to those formerly applied ¹⁾.

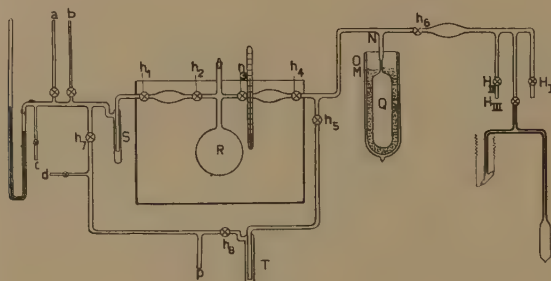


Fig. 2.

To prevent, that considerable errors would occur in the calibration of the hot wire manometers in consequence of thermomolecular pressure differences, because one part of the capillary DE is at room temperature another part being kept at 0° C., the bulb Q , which contains the largest part (ca. 96 %) of the volume, is immersed too in a bath of ice and distilled water. The connecting tube MON consists of two parts, of which the one MO has exactly the same diameter as the capillary of the thermometers I and II, whereas the diameter of the other part ON is exactly the same as that of the capillary of thermometer III. At the calibration of the hot wire manometers I and II the level in the ice-bath surrounding Q is kept at the

¹⁾ Comp. Comm. Leiden Nos 137b and 150a.

part *MO*, and at the calibration of manometer III at the part *ON*. In this convenient way we took care, that the correction, caused by the thermomolecular pressure difference, at the calibration of the hot wire manometer in ice is very small and may practically be neglected.

Though the electrical constants of the Wollastonwire and likewise the temperature of the bath, in which they were immersed, remained very constant, yet it turned out that the calibrations of the hot wire manometers undergo changes in the course of time. So it is necessary to control the calibrations regularly. The differences before and after the measurements in liquid helium, for which it was necessary to remove the apparatus to another room, are in general of the order of 1 % at the utmost. These changes put a limit to the absolute accuracy of the experiments. The relative accuracy, however, is much greater.

Since these changes in the calibrations are not to be ascribed to changes in the electrical constants, it is very likely that they must be due to changes at the surface of the hot wire, probably by the formation of gas films at the surface, through which the accommodation coefficient of the helium with regard to the wire changes.

Especially for a gas with a very small accommodation coefficient¹⁾, such as helium and hydrogen, we must expect, that a small change at the surface may have an important influence on the heat transfer. This view is supported also by some experiments, where first the hot wire had been annealed during some time, for here it turned out that the variations were larger directly after the annealing, and also, just as in our experiments, always went in one direction. Since we could not quite avoid taps and grease in our installation, we have not annealed the hot wire.

In order to eliminate the influence of such changes in the calibration we have, after the results have been corrected for the thermomolecular pressure difference, shifted the vapour pressure curves, obtained at several series of measurements, so as to coincide at the boiling point $T = 4.22^\circ \text{K}$. As appears from the tables below those shifts are very small.

§ 3. *The correction for the thermomolecular pressure difference.* This is the most important correction, which is to be taken in consideration at the determination of the temperature of liquid helium at the lowest temperatures. It can get so large, that all other corrections compared with it may be neglected. In Comm. N^o. 147*b* the authors gave a detailed discussion concerning this correction, and for lack of experimental data tried to improve the theory of it. Till now however the necessary experimental data are not yet at our disposal. It is our intention to have an extensive research performed while using the gas thermometer itself. If namely the thermometer is filled with known quantities of gas and then immersed in a bath of *known* temperature, then we get a direct measurement of the influence

¹⁾ M. KNUDSEN. *Ann. d. Phys.* (4) 46, 641, 1915.

of the thermomolecular pressure difference on the determination of the temperature, and so also a measurement of the thermomolecular pressure difference. This method, which we already used for a series of preliminary measurements in liquid oxygen and hydrogen, has the advantage, compared with the methods followed until now ¹⁾, that the determination is made with one capillary and not, as otherwise, by a measurement of the difference between a wide and a narrow tube. This is in particular of great importance at the determination of the thermomolecular pressure difference in the neighbourhood of the limiting condition $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$.

After that method we have performed some preliminary measurements for helium also and though this material is only suitable for a first survey, yet it is sufficient to calculate the corrections for the measurements published in the following tables.

§ 4. *The measurements of the vapour pressure of the liquid helium* was done in two ways: 1st, by measuring the pressure in the cryostat above the level of the slowly evaporating helium, and 2nd, by measuring the vapour pressure above the liquid helium in an open tube, which reached into the liquid helium. In this way the pressure was measured above the liquid helium level, where evaporation takes place, and on the other hand above the same helium, where no evaporation takes place. It turned out, that within the experimental accuracy the agreement between the two determinations was sufficient down to a vapour pressure of about 0.5 cm. mercury. Below this vapour pressure the accuracy of the mercury manometers was not sufficient. Therefore we later used, as will be shown in the next communication on this subject, for the lower vapour pressures other vapour pressure tubes and other manometers. At the lower vapour pressures it is also necessary to use vapour pressure tubes with exactly known diameters, because the corrections for the thermomolecular pressure differences in the vapour pressure tube grow important there.

We give the pressures in centimeters mercury of 0° C. at normal gravity.

§ 5. *The results of the measurements* are given in the following tables: (See tables on the following pages.)

In these tables I, II and III:

$T_{I,a}$ and $T_{III,a}$ are the temperatures calculated from the measurements, the corrections for the noxious volume, determined by the measurements with thermometer II (auxiliary capillary), and the corrections for the thermal contraction of the bulbs ²⁾ having been made.

$T_{I,b}$ and $T_{III,b}$ have been derived from the values of $T_{I,a}$ and $T_{III,a}$, by

¹⁾ M. KNUDSEN. *Ann. d. Phys.* (4) 31, 205, 1910 and (4) 83, 797, 1927.

²⁾ F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES. *These Proceedings* 28, 667, 1925; *Comm. Leiden* N°. 176a. *Comp. Comm. Leiden* N°. 188a, p. 6.

applying, on account of our preliminary measurements (see § 3), the corrections for the thermomolecular pressure differences.

$T_{I,c}$ and $T_{III,c}$ have been derived from $T_{I,b}$ and $T_{III,b}$ by bringing the calibrations of the hot wire manometers in agreement with the boiling point $T = 4.22^\circ \text{K}$.

TABLE I.
Measurements December 16th 1927.
Icepoint pressures:
Thermometers I and III: $p_0 = 9.955 \text{ cm. Hg.}$
" II : $p_0 = 0.880 \text{ cm. "}$

| Vapour pressure p cm. Hg. | $T_{I,a}$ | $T_{III,a}$ | $T_{I,b}$ | $T_{III,b}$ | $T_{I,c}$ | $T_{III,c}$ |
|-----------------------------------|-----------|-------------|-----------|-------------|-----------|-------------|
| 78.47 | 4.265 | 4.292 | 4.232 | 4.292 | 4.255 | 4.255 |
| 35.00 | 3.514 | 3.524 | 3.472 | 3.519 | 3.491 | 3.489 |
| 16.47 | 2.969 | 2.969 | 2.916 | 2.962 | 2.932 | 2.936 |
| 6.950 | 2.498 | 2.478 | 2.433 | 2.466 | 2.446 | 2.445 |
| 4.633 | 2.316 | 2.316 | 2.246 | 2.302 | 2.258 | 2.283 |
| 4.061 | 2.263 | 2.273 | 2.193 | 2.258 | 2.205 | 2.239 |
| 3.763 | 2.225 | 2.194 | 2.156 | 2.179 | 2.168 | 2.161 |
| 3.494 | 2.200 | 2.168 | 2.130 | 2.153 | 2.141 | 2.134 |
| 3.192 | 2.168 | 2.138 | 2.096 | 2.121 | 2.107 | 2.103 |
| 2.655 | 2.103 | 2.070 | 2.029 | 2.053 | 2.040 | 2.036 |
| 1.974 | 2.007 | 1.968 | 1.929 | 1.949 | 1.939 | 1.932 |
| 1.020 | 1.817 | 1.778 | 1.735 | 1.757 | 1.744 | 1.742 |

TABLE II.
Measurements December 21st 1927.
Icepoint pressures for I, II and III the same as on December 16th 1929.

| Vapour pressure p cm. Hg. | $T_{I,a}$ | $T_{III,a}$ | $T_{I,b}$ | $T_{III,b}$ | $T_{I,c}$ | $T_{III,c}$ |
|-----------------------------------|-----------|-------------|-----------|-------------|-----------|-------------|
| 76.85 | 4.280 | 4.297 | 4.247 | 4.297 | 4.232 | 4.232 |
| 3.982 | 2.264 | 2.281 | 2.194 | 2.266 | 2.186 | 2.232 |
| 3.746 | 2.231 | 2.269 | 2.162 | 2.254 | 2.154 | 2.220 |
| 3.668 | 2.220 | 2.246 | 2.152 | 2.232 | 2.145 | 2.198 |
| 0.994 | 1.811 | 1.761 | 1.729 | 1.739 | 1.723 | 1.712 |

TABLE III.
Measurements January 20th 1928.
Icepoint pressures:
Thermometers I and III: $p_0 = 5.4615$ cm. Hg.
" II : $p_0 = 1.029$ " "

| Vapour pressure p cm. Hg. | $T_{I,a}$ | $T_{III,a}$ | $T_{I,b}$ | $T_{III,b}$ | $T_{I,c}$ | $T_{III,c}$ |
|-----------------------------------|-----------|-------------|-----------|-------------|-----------|-------------|
| 78.22 | 4.377 | 4.321 | 4.254 | 4.293 | 4.246 | 4.246 |
| 35.13 | 3.635 | 3.562 | 3.490 | 3.526 | 3.483 | 3.488 |
| 16.10 | 3.072 | 2.989 | 2.918 | 2.944 | 2.912 | 2.912 |
| 7.095 | 2.617 | 2.531 | 2.449 | 2.478 | 2.444 | 2.451 |
| 3.645 | 2.325 | 2.230 | 2.157 | 2.170 | 2.153 | 2.146 |
| 2.006 | 2.105 | 2.015 | 1.920 | 1.947 | 1.916 | 1.925 |
| 1.006 | 1.911 | 1.812 | 1.724 | 1.739 | 1.720 | 1.720 |

As appears from the tables the corrections are not very important in these measurements.

The correction for the thermal contraction of the bulb is about $\frac{1}{2}\%$.

The correction for the noxious volume depends on the distribution of temperature in the cryostat, but it is eliminated by means of the auxiliary capillary. It would amount for thermometer I to $\pm 1.5\%$ and for thermometer III to 4% at the boiling point of helium. At lower temperatures it is still smaller.

The corrections for the thermomolecular pressure differences are as follows:

In the measurements of December 16th and 21st 1927, where the icepoint pressure amounted to about 10 cm.:

| vapour pressure p | corrections in the temperature | |
|------------------------|--------------------------------|-----------|
| | T_I | T_{III} |
| 76 cm. | ca. 0.6% | $< 0.1\%$ |
| 1 " | ca. 4.5% | 1.5% ; |

for the measurements on January 20th 1928, where the icepoint pressure amounted to about 5 cm.:

| | | |
|--------|------------|---------|
| 76 cm. | ca. 3% | 0.8% |
| 1 " | ca. 10% | 4.0% |

The corrections because of the deviation of helium from the Avogadro-state may be neglected in this investigation, for according to the researches of KAMERLINGH ONNES and BOKS ¹⁾ we have for helium:

$$B_{4.22^\circ \text{K.}} = -0.00007,$$

¹⁾ Comp. C. A. CROMMELIN. Comm. Leiden Suppl. N^o. 63, p. 21.

and extrapolating

$$B_{1.50^\circ \text{K.}} = -0.00009.$$

From this we find as a maximum in our measurements at $T = 4.22^\circ \text{K.}$

$$\frac{T_{\text{corr. } B}}{T} = 1 + 0.0006,$$

and at $T = 1.50^\circ \text{K.}$:

$$\frac{T_{\text{corr. } B}}{T} = 1 + 0.0022.$$

These corrections may be neglected.

§ 6. In Fig. 3 the results of the tables I, II and III are represented in a logarithmic diagram; the ordinate is $\log_{10} p_{\text{cm}}$ and the abscissa $\frac{1}{T}$. The points agree very well with the curve and the agreement between the separate series is very satisfactory. From the curve, drawn through the points, we have read some points which are mentioned in table IV. These values, joined to those of a following communication which deals on

TABLE IV.
Comp. Fig. 3.

| Vapour pressure p cm. Hg. | $T, ^\circ\text{K.}$ | $\log_{10} p$ cm. Hg. | $\frac{1}{T}, ^\circ\text{K.}$ |
|-----------------------------------|----------------------|--------------------------|--------------------------------|
| 76.00 | 4.22 | 1.881 | 0.237 |
| 50.00 | 3.79 | 1.700 | 0.264 |
| 25.00 | 3.21 | 1.398 | 0.312 |
| 10.00 | 2.63 | 1.000 | 0.380 |
| 5.00 | 2.29 | 0.700 | 0.436 |
| 2.50 | 2.01 | 0.398 | 0.497 |
| 1.00 | 1.72 | 0.000 | 0.581 |

measurements of the vapour pressure curve between $T = 1.70^\circ \text{K.}$ and 1.15°K. will be discussed later in connection with the known vapour pressure formulæ.

§ 7. *The transformation He I—He II.* According to the temperature scale given by Fig. 3 and table IV the transformation point *He I—He II.* for which in Comm. N^o. 192a $p = 3.865 \text{ cm.}$ was found, lays at 2.18°K. ($\frac{1}{T} = 0.459$).

In Fig. 3, the discontinuity, which the vapour pressure curve, on account of the transformation heat (Comm. N^o. 190*b* § 2*b*) must show in its slope,

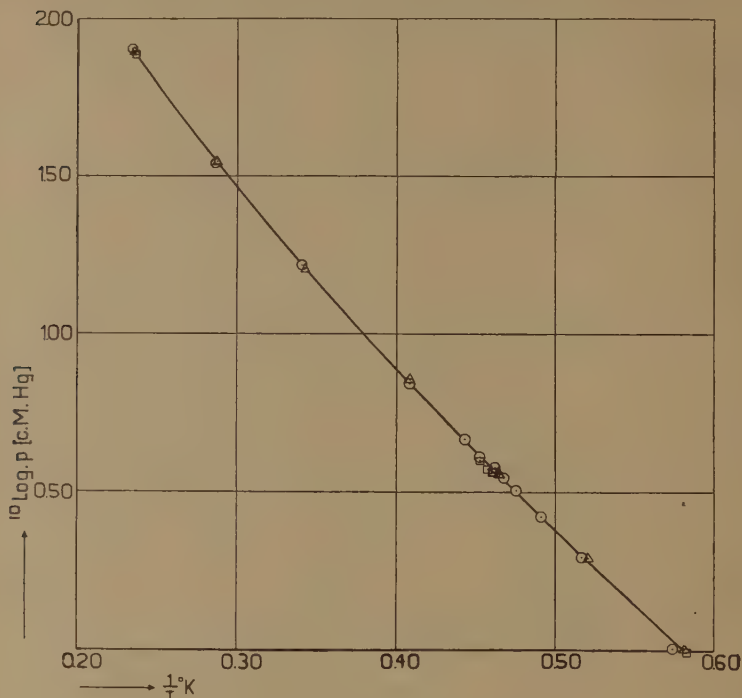


Fig. 3.

- Average of T_{Ic} and T_{IIIc} , table I.
 □ " " " " " " " II.
 △ " " " " " " " III.

is not to be recognized with certainty. As a matter of fact, a calculation based on the value of the transformation heat shows that the discontinuity is so small, that in connection with the experimental errors this cannot be expected.

Meanwhile also at this investigation the existence of the transformation He I—He II appeared obvious from two heating curves obtained by registration of the deviation of the galvanometer, which is placed in the Wheatstone bridge, in which the hot wire manometer of the thermometer I is taken up, when the cryostat bath, after having been cooled below the transformation point, heated slowly. One of these curves has already been published in Comm. N^o. 190*b* Fig. 2. We give them both with indication of the temperature in Fig. 4. These curves both give an obvious indication

for the transformation, but they give no data for a more exact determination of the transformation temperature. This can better be calculated, as is done

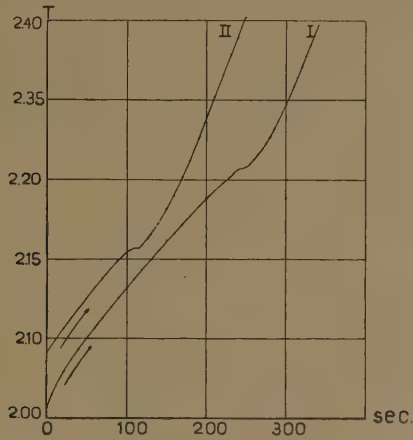


Fig. 4.

Curve I. Registered December 16th, 1927.

" II. , " " 21st, "

above, from the transformation pressure, which was measured statically.

Finally we wish to thank Mr. G. SCHMIDT, assistant at the Physical Laboratory of Leiden, for his assistance in calculating the results.

Physics. — *Disturbance of the superconductivity of the compound Bi_5Tl_3 and of the alloys Sn-Sb and Sn-Cd by magnetic fields.* By W. J. DE HAAS and J. VOOGD. (Comm. N^o. 199c from the Phys. Lab. at Leiden).

(Communicated at the meeting of September 28, 1929).

In collaboration with Prof. E. VAN AUBEL we found, that the compound Bi_5Tl_3 already becomes superconductive above the boiling point of helium (4.2°K.) ¹⁾. We now tried to determine its magnetic threshold value at the boiling point of helium. This threshold value proved to lie so high, that the solenoid always used in the other experiments (H up to 1250 gauss) did not suffice, so that we were obliged to use an electromagnet to reach field intensities strong enough to disturb the supraconductivity.

The compound Sb_2Tl_7 too, which becomes superconductive above 4.2°K. , demands a field higher than 1250 G. to disturb its superconductivity at 4.2°K. ²⁾. The further investigation of the magnetic disturbance of the superconductivity of Bi_5Tl_3 showed, that the fall of the magnetic threshold value with decreasing temperature is much steeper here than for pure superconductors.

In order to find out whether this also is a general property of alloys, we chose for the further research solid solutions of bismuth in tin and of cadmium in tin and especially used the eutectics of the systems Sn-Bi and Sn-Cd . In collaboration with Prof. E. VAN AUBEL we had already investigated these solid solutions with respect to the temperature transition point (thermal transition curve) ³⁾.

§ 2. Bi_5Tl_3 .

We worked with the rod that had also been used the second time for the investigation of the resistance ⁴⁾. This rod was mounted in a removable helium cryostat which after having been filled with liquid helium was placed between the pole pieces (diameter 16 cm.) of an electro-magnet (type Weiss, Oerlikon make). The field intensity was measured ballistically. Also the inhomogeneity was investigated and it proved to be less than 1 % along the rod.

¹⁾ These Proceedings, **32**, 218, 1929.

²⁾ These Proceedings, **32**, 731, 1929. Comm. Leiden 197d.

³⁾ These Proceedings, **32**, 715, 1929. Comm. Leiden 197b.

⁴⁾ These Proceedings, **32**, 731, 1929. Comm. Leiden 197d.

We give the results of these determinations in table I and in fig. 1.

TABLE I.
 $Bi_5 Tl_3$ (magnetic field transversal).

| H | R | T | P |
|------|----------|-------------------|-----|
| 3865 | 0 | 4.20 ⁸ | 766 |
| 4038 | 0.000221 | | |
| 4151 | 0.000436 | | |
| 4181 | 0.000496 | | |
| 4254 | 0.000582 | | |
| 4634 | 0.000597 | | |
| 4149 | 0 | 4.03 ⁸ | 647 |
| 4240 | 0.000058 | | |
| 4283 | 0.000158 | | |
| 4392 | 0.000350 | | |
| 4627 | 0.000594 | | |
| 4851 | 0.000594 | | |
| 5836 | 0.000604 | | |
| 4402 | 0 | 3.88 ⁴ | 549 |
| 4654 | 0.000245 | | |
| 4773 | 0.000480 | | |
| 4874 | 0.000579 | | |
| 5245 | 0.000597 | | |
| 5049 | 0.000134 | 3.61 ¹ | 399 |
| 5275 | 0.000471 | | |
| 5405 | 0.000579 | | |
| 5577 | 0.000594 | | |
| 5868 | 0.000594 | | |
| 5423 | 0.000087 | 3.39 ⁰ | 299 |
| 5575 | 0.000342 | | |
| 5961 | 0.000595 | | |
| 5846 | 0.000585 | | |

From the figure we can find the value of the magnetic field, for which the resistance is restored to half of its original value ($H_{W1/2}$). In table II

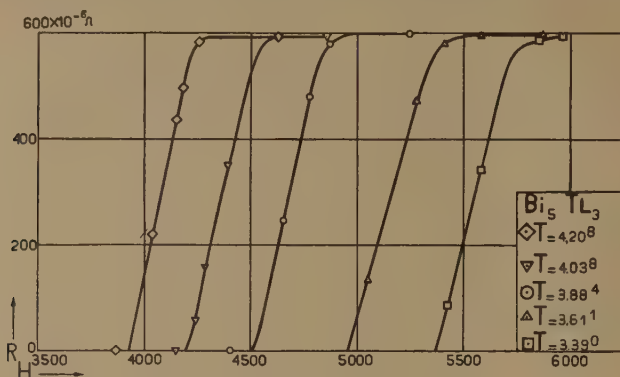


Fig. 1.

the values of $H_{W1/2}$ are given for the different temperatures. Fig. 2 represents the curve of $H_{W1/2}$ as a function of the temperature. For comparison this same curve has been plotted for pure lead (derived from the determinations of W. TUYN and H. KAMERLINGH ONNES¹⁾).

We see, that the inclination of this curve is much steeper for Bi_5Tl_3 than for lead.

By extrapolation we can make from the figure an estimate of the transition point of Bi_5Tl_3 , for which we find approximately 6.5°K .

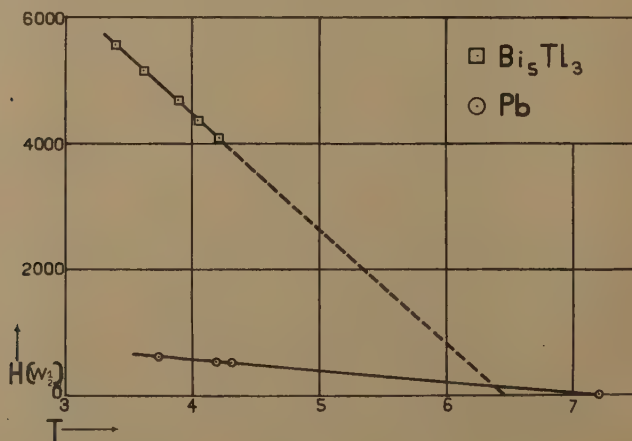


Fig. 2.

¹⁾ Comm. Leiden 174a. Journal of the Franklin Institute, 201, 379, 1926.

TABLE II.

 $Bi_5 Tl_3$.

| $Hw^{1/2}$ | T |
|------------|-------------------|
| 4080 | 4.20 ⁸ |
| 4360 | 4.03 ⁸ |
| 4680 | 3.88 ⁴ |
| 5150 | 3.61 ¹ |
| 5560 | 4.39 ⁰ |

§ 3. *Sn-Bi*.

We worked with a rod of the eutectic mixture, which according to the melting point diagram consists of a solid solution of bismuth in tin and a solid solution of tin in bismuth. The superconductivity of the rod is a consequence of the continuity of the layers of the solid solution of bismuth in tin and the magnetic transition figure must be ascribed to this solid solution ¹⁾.

The longitudinal fields were obtained by means of a solenoid surrounding the helium cryostat. In table III we give the determinations of the magnetic transition figures, plotted in fig. 3.

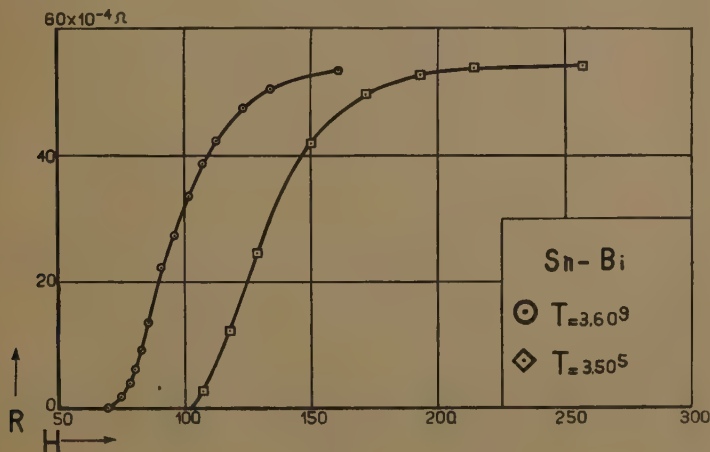


Fig. 3.

We see, that the magnetic field in which the return of the resistance

¹⁾ These Proceedings, 32, 715, 1929. Comm. Leiden 197b.

TABLE III.

Sn—Bi.

| <i>H</i> | <i>R</i> | <i>T</i> | <i>p</i> |
|----------|----------|-------------------|----------|
| 69.5 | 0.000017 | 3.60 ⁹ | 398 |
| 74.9 | 0.000168 | | |
| 78.1 | 0.000392 | | |
| 80.3 | 0.000613 | | |
| 82.6 | 0.000902 | | |
| 85.6 | 0.001357 | | |
| 91.0 | 0.002225 | | |
| 96.3 | 0.002731 | | |
| 101.7 | 0.003351 | | |
| 107.0 | 0.003861 | | |
| 112.4 | 0.004233 | | |
| 123.1 | 0.004748 | | |
| 133.8 | 0.005055 | | |
| 160.5 | 0.005351 | | |
| 107.0 | 0.003845 | | |
| 80.3 | 0.000617 | 3.50 ⁵ | 349 |
| 107.0 | 0.000262 | | |
| 117.7 | 0.001227 | | |
| 128.4 | 0.002440 | | |
| 149.8 | 0.004181 | | |
| 171.2 | 0.004962 | | |
| 192.6 | 0.005274 | | |
| 214.0 | 0.005380 | | |
| 256.8 | 0.005425 | | |
| 171.2 | 0.004968 | | |
| 117.7 | 0.001223 | | |

begins and that in which the resistance has reached again its original value, lie at a great distance.

This must be ascribed, if not wholly then at all events partly to the fact,

that the current has to choose its path through the differently orientated layers of the solid solution and that the current vector has all directions

We have therefore to do both with the transverse and with the longitudinal action of the magnetic field.

In table IV we give the values of $H_{W1/2}$ with the corresponding temperatures.

TABLE IV.

Sn—Bi.

| $H_{W1/2}$ | T |
|------------|-------------------|
| 95 | 3.60 ⁹ |
| 130 | 3.50 ⁵ |

In fig. 5 these values have been plotted with those of *Sn—Cd* and those of pure tin¹⁾ (derived from the determinations of W. TUYN and H. KAMERLINGH ONNES).

It is seen, that for *Sn—Bi* the values of $H_{W1/2}$ increase more rapidly with decreasing temperature than for pure tin.

§ 4. *Sn—Cd.*

Here too we worked with a rod of the eutectic mixture, in which it is the solid solution of cadmium in tin that becomes superconductive²⁾.

In the same way as for *Sn—Bi* the magnetic transition curves were determined here. The results are given in table V and are plotted in fig. 4. With respect to the form of the transition figures the same remarks may

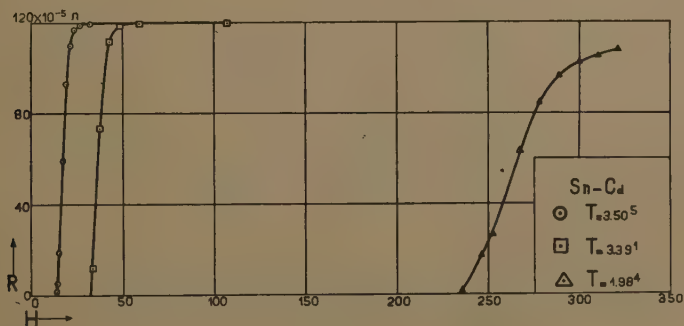


Fig. 4.

¹⁾ Comm. Leiden 174a. Journal of the Franklin Institute, **201**, 379, 1926.

²⁾ These Proceedings, **32**, 715, 1929. Comm. Leiden 197b.

TABLE V.
Sn—Cd.

| <i>H</i> | <i>R</i> | <i>T</i> | <i>p</i> |
|----------|----------|-------------------|----------|
| 12.84 | 0 | 3.50 ⁵ | 349 |
| 13.27 | 0.000016 | | |
| 13.91 | 0.000051 | | |
| 14.98 | 0.000187 | | |
| 17.12 | 0.000594 | | |
| 19.26 | 0.000931 | | |
| 21.40 | 0.001100 | | |
| 23.54 | 0.001169 | | |
| 26.75 | 0.001190 | | |
| 32.10 | 0.001195 | | |
| 21.40 | 0.001108 | | |
| 17.12 | 0.000605 | | |
| 13.91 | 0.000059 | | |
| 33.2 | 0.000118 | 3.39 ¹ | 299 |
| 37.5 | 0.000734 | | |
| 42.8 | 0.001116 | | |
| 48.2 | 0.001186 | | |
| 64.2 | 0.001197 | | |
| 107.0 | 0.001197 | | |
| 42.8 | 0.001127 | | |
| 37.5 | 0.000736 | | |
| 32.1 | 0.000040 | | |
| 235.4 | 0.000019 | 1.98 ⁴ | 17.0 |
| 246.1 | 0.000131 | | |
| 252.5 | 0.000265 | | |
| 267.5 | 0.000634 | | |
| 278.2 | 0.000847 | | |
| 288.9 | 0.000964 | | |
| 299.6 | 0.001023 | | |
| 310.3 | 0.001053 | | |
| 321.0 | 0.001079 | | |
| 288.9 | 0.000965 | | |
| 267.5 | 0.000634 | | |
| 246.1 | 0.000123 | | |

be made as in the case of *Sn-Bi*. Table VI gives the values of $H_{W^{1/2}}$, which have been plotted in fig. 5.

TABLE VI.
Sn—Cd.

| $H_{W^{1/2}}$ | T |
|---------------|-------------------|
| 17.5 | 3,50 ⁵ |
| 36 | 3,91 ¹ |
| 266 | 1,98 ⁴ |

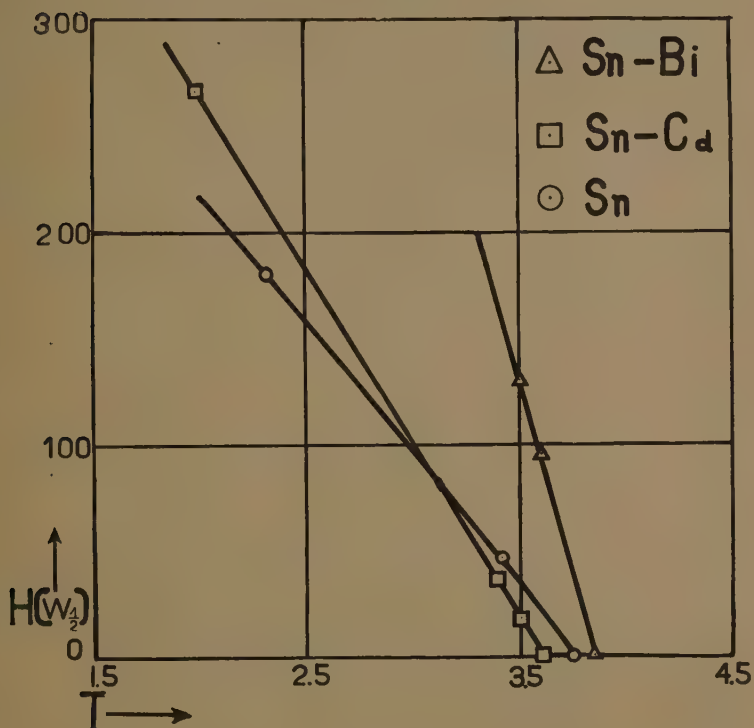


Fig. 5.

The difference with pure tin is less pronounced which may be ascribed perhaps to the fact, that in the eutectic *Sn-Cd* the percentage of cadmium is considerably lower than that of bismuth solved in tin in the eutectic *Sn-Bi*.

§ 5. The result of these measurements with alloys is, that in all cases

investigated the value of $H_{W^{1/2}}$ increases more rapidly with decreasing temperature than in the case of the pure superconductors. We can also express this by saying, that for the same temperature distance from the transition point higher field intensities are required to restore the resistance. This unexpected result may become of use in magnetic researches because of the high values of $H_{W^{1/2}}$ found for Bi_5Tl_3 .

We found, that at 3.4° K. a field of 5.3 kilogauss did not yet disturb the superconductivity of Bi_5Tl_3 . We have not yet extended our investigations to still lower temperatures. An extrapolation however of the data would predict that at a temperature of 1.3° K. a field of about 9 kilogauss would not yet disturb the superconductivity. *This would render possible the production of magnetic fields of this order of magnitude with a solenoid from Bi_5Tl_3 wire without production of heat.* It is evident however, that besides this eventual practical application, the phenomenon itself is of the highest importance.

Physics. — *Zur Thermodynamik und Kinetik der thermo-elektrischen Erscheinungen in Krystallen, insbesondere des BRIDGMAN-Effektes, II.* Von P. EHRENFEST und A. J. RUTGERS.

(Communicated at the meeting of September 28, 1929).

Einleitung. Im Anschluss an die thermodynamische Behandlung des BRIDGMAN-Effektes im Theil I, versuchen wir nun klarzustellen, welche Annahmen fuer eine *kinetische* Deutung dieses Effektes wesentlich sind.

Am BRIDGMAN-Effekt ist so ueberraschend, dass eine reversible Waermentwicklung an Stellen auftritt, wo die den Strom tragenden Elektronen innerhalb desselben homogenen und uniform temperierten Mediums bleiben. In der klassischen Elektronentheorie, wie sie insbesondere durch LORENTZ ¹⁾ dargestellt wurde, beruht ja die PELTIER-Waerme ausschliesslich auf der *Kompression des Elektronengases* beim Uebergang der stromtragenden Elektronen ueber die Grenze zweier Leiter mit verschiedenen Elektronendichten; in dem uniform temperierten Krystall aber ist die Elektronendichte ueberall gleich.

Merkwuerdigerweise genuegt aber schon eine geringe Modifikation in den Grundannahmen der LORENTZschen Theorie, um den BRIDGMAN-Effekt zu erhalten, und zwar auch dann, wenn man die klassische Geschwindigkeitsvertheilung der Elektronen beibehalten wuerde. Es genuegt naemlich die folgende zweistufige Annahme:

A. Die mittlere freie Weglaenge eines Elektrons haengt von seiner Geschwindigkeit ab. ²⁾

B. Diese Abhaengigkeit ist verschieden fuer verschiedene Bewegungsrichtungen innerhalb des Krystalls. ³⁾

¹⁾ H. A. LORENTZ. The motion of electrons in metallic bodies I, II, III. These Proceedings, Vol. 7, 438, 585, 684, 1905. Im Folgenden zitiert als [A].

Le mouvement des électrons dans les métaux. Arch. Néerl. Série II, Tome X, 336, 1905. Im Folgenden zitiert als (B).

Anwendung der kinetischen Theorien auf Elektronenbewegung. Math. Vorl. an der Univ. Goettingen VI, 167, 1914. (Wolfskehlvortraege). (Im Folgenden zitiert als (C)).

²⁾ In Verbindung mit speziellen Vorstellungen bei P. GRUNER, Verh. der deutschen phys. Ges. 10 (13), 509, 1908, und phys. Zeitschr. 10, 48, 1909 auftretend. BOHR hat in seiner Dissertation: Studier over Metallernes Elektrontheori, (Kobenhavn 1911) mit der Annahme gerechnet, dass die Elektronen durch die Metallatome nach Kraftgesetz r^{-n} angezogen werden, was eine mit n veraenderliche Abhaengigkeit der freien Weglaenge von der Geschwindigkeit gibt. — Siehe auch z.B. O. W. RICHARDSON, Some Applications of the Electron Theory of Matter, Phil. Mag. (6), 23, 594, 1912. — SOMMERFELD, l.c. S. 19, laesst beliebige Abhaengigkeit $1/v$ zu. HOUSTON, Elektrische Leitfaehigkeit auf Grund der Wellenmechanik, Z. f. Ph. 48, 449, 1928, bestimmt $1/v$ aus der Beugung von Elektronenwellen an den Metallionen.

³⁾ Als erster scheint HOUSTON l.c. S. 461 von der Annahme B Gebrauch gemacht zu haben, und zwar berechnet er die Wahrscheinlichkeit, dass eine Elektronenwelle mit den Momenten $p_0 q_0 r_0$ durch ein anisotropes Ionengitter nach pqr abgelenkt wird.

Die thermoelektrische Bedeutung der Annahme (A) kann man sich am bequemsten an dem folgenden uebertriebenen Modell deutlich machen: Man betrachte den Stromuebergang zwischen zwei gleichwarmen Leitern mit gleicher Elektronendichte.¹⁾ Die mittlere freie Weglaenge, also Beweglichkeit sei fuer die Elektronen aller Absolutgeschwindigkeiten sehr klein, ausgenommen fuer die der Geschwindigkeit v_I im linken Leiter und die Geschwindigkeit v_{II} im rechten Leiter. Fuer diese beiden Gruppen sei die Weglaenge, Beweglichkeit sehr gross. Ein durch die Grenzflaeche gehender Strom wird also links fast ganz durch „ v_I -Elektronen“ herangebracht, und rechts durch ebensoviele „ v_{II} -Elektronen“ (keine Anhaeufung von Elektrizitaet) abtransportiert. Ist also z. B. $v_I > v_{II}$, so wird per Elektron an der Grenze die Energie $\frac{m}{2} (v_I^2 - v_{II}^2)$ reversibel frei-

kommen, und muss als PELTIERwaerme in ein Waermereservoir abgefuehrt werden, um die Temperatur constant zu halten. Unser Modell laesst also sehen: Die Annahme (A) liefert — auch schon bei klassischer Statistik — eine zweite Quelle fuer PELTIERwaerme²⁾ neben der bei LORENTZ allein beruecksichtigten Kompressionswaerme.

Nun ist auch plausibel, wie die Annahme (B) die kinetische Deutung der Peltierwaerme ($\pi_{\perp||}$) an der Grenzflaeche von zwei senkrecht zueinander orientierten Stuecken desselben Krystalls ermoeeglicht: Der elektrische Strom wird im Mittel durch Elektronen anderer kinetischer Energie transportiert, wenn er \perp oder \parallel zur Hauptaxe des Krystalls fliesst. Somit tritt auch an einer ($\perp \parallel$)-Grenze der selben Krystallsubstanz Aufstauung kinetischer Energie fuer die den Strom an- und ab-transportierenden Elektronen auf.

Beim BRIDGMAN-Effekt findet dann diese Aufstauung kontinuierlich statt, entsprechend der kontinuierlichen Richtungsaenderung der Stromlinien.

Allgemein laesst sich die Wirkung der Annahmen (A) (B) etwa folgendermassen anschaulich beschreiben: Im Innern eines homogenen, uniform temperierten, stromlosen Krystalls ist die Geschwindigkeitsvertheilung centrisc symmetrisch fuer die Elektronen jeder einzelnen Absolutgeschwindigkeit $v_{\alpha}, v_{\beta}, v_{\gamma}, v_{\delta}, \dots$. Fliesst aber unter der Wirkung eines beliebig schief gerichteten elektrischen Feldes ein Strom — der Einfachheit halber sei die Temperatur uniform — so ist die Richtungsvertheilung fuer

¹⁾ Also auch mit gleicher mittlerer kinetischer Energie der Elektronen, wenn man mit der klassischen Statistik oder mit derjenigen rechnet, die SOMMERFELD benuetzt. Von dem Einfluss auch noch der Atomfelder auf die Quantisierung und damit auf die Statistik (siehe BLOCH: Quantenmechanik der Elektronen in Krystallgittern. Z. f. Ph. 52, 555, 1929) sei also hier abgesehen.

²⁾ BOHR, l.c., S. 67.

P. GRUNER, Phys. Zeitschr. 10, S. 49, Formel (18), 1909.

A. SOMMERFELD, Z. f. Ph. 47, S. 46, Formel (61c), 1928.

die Elektronen irgend einer Absolutgeschwindigkeit v , nicht mehr centrisch symmetrisch, sondern verweht, und zwar fuer die verschiedenen Absolutgeschwindigkeiten v_α , v_β wegen der Annahmen (A) (B) verschieden stark und verschieden schief gegen die Richtung des Feldes. (Besonders stark fuer grosse freie Weglaenge). Die verwehte Gruppe v_1 liefert einen Beitrag zum elektrischen Strom und einen damit gleichgerichteten und proportionalen Beitrag zum Transport der kinetischen Energie. Analog die anders verwehte Gruppe v_2 , und so weiter. Da aber der Proportionalitaetsfaktor sich mit v aendert liegt die Vektorsumme fuer die Beitrage zur Stroemung der kinetischen Energie schief zum resultierenden Strom. So wird verstaendlich, dass die Annahmen (A) (B) eine kinetische Deutung des Phaenomens ermoeglichen, dass der elektrische Strom in einem Krystall mit einer schief zu ihm stehenden reversibeln Entropiestroemung verknuepft erscheint. (Siehe I, § 8 II, § 7).

§ 1. Die Grundannahmen moegen hierbei — abgesehen von der Einfuehrung der Anisotropie — die sein, mit denen die Sommerfeldsche Theorie der Metallelektronen rechnet, und sie umfassen also als Grenzfall auch die der Lorentzschen Theorie. Es werden also die Zusammenstoesse der Elektronen untereinander nicht beruecksichtigt; fuer die mit den Metallatomen wird wie bei LORENTZ und SOMMERFELD so gerechnet, also beim einzelnen Zusammenstoss das Elektron wohl die Bewegungsrichtung, aber nicht den Betrag der Geschwindigkeit aendert:¹⁾

$$v'^2 = \xi'^2 + \eta'^2 + \zeta'^2 = \xi^2 + \eta^2 + \zeta^2 = v^2 \quad . \quad . \quad . \quad (27)$$

Bezuglich dieser Zusammenstoesse machen wir ferner ausdruücklich die Annahme: Zu jedem Stoss $a_1 a_2 a_3 \rightarrow a'_1 a'_2 a'_3$ (er heisse der „direkte“) existiert auch stets der zugehoerige „restituierende“ Stoss $a'_1 a'_2 a'_3 \rightarrow a_1 a_2 a_3$ und ueberdies: Der Faktor, der bei gegebenem v die Wahrscheinlichkeit verschiedener Richtungsspruenge $a_1 a_2 a_3 \rightarrow a'_1 a'_2 a'_3$ bestimmt ist fuer den direkten und restituierenden Stoss gleich gross; genauer formuliert: Wir nehmen an: In der bekannten BOLTZMANN-LORENTZschen Bedingungsgleichung fuer Stationaritaet der Zustandsvertheilung $f(x_1 x_2 x_3, \xi_1 \xi_2 \xi_3)$ der Elektronen:

$$\frac{\partial f}{\partial \xi_r} \frac{eF_r}{m} + \frac{\partial f}{\partial x_r} \xi_r = \int d\omega' W(xv; a' a) f(x, \xi') - \left\{ \int d\omega' W(xv; a a') f(x, \xi) \right\} \quad . \quad . \quad (28)$$

besitzt der Faktor W die Symmetrieeigenschaft:

$$W(xv; a'_1 a'_2 a'_3, a_1 a_2 a_3) = W(x, v; a_1 a_2 a_3, a'_1 a'_2 a'_3). \quad . \quad (29)$$

Dann laesst sich der rechtsstehende Stossterm (restituierende minus

¹⁾ Siehe Fussnote § 5.

direkte Stoesse) auf die (fuer die Ableitung z.B. des H -Theorems so charakteristische) Form bringen: ¹⁾

$$\frac{\partial f}{\partial \xi_r} \frac{eF_r}{m} + \frac{\partial f}{\partial x_r} \xi_r = \int d\omega' W(x, v; a' a) \{f(x, \xi') - f(x, \xi)\} \quad (30)$$

wobei $\frac{eF_1}{m} \frac{eF_2}{m} \frac{eF_3}{m}$ die Komponenten der Beschleunigung eines Elektrons bezeichnen.

Ferner nehmen wir an, dass die Zustandsvertheilung $f(x, \xi)$ (wegen des Temperaturgefalles und der elektrischen Kraft) durch eine *kleine* Störung $g(x, \xi)$:

$$f(x_1 x_2 x_3, \xi_1 \xi_2 \xi_3) = f_0(x_1 x_2 x_3, \xi_1 \xi_2 \xi_3) + g(x_1 x_2 x_3, \xi_1 \xi_2 \xi_3) \quad (31)$$

von derjenigen Vertheilung f_0 abweicht, die in einem stromlosen homogenen Krystall herrschen wuerde, wenn dieser *ueberall* gerade diejenige Temperatur und Struktur besaesse, die hier im Punkte $x_1 x_2 x_3$ vorhanden ist.

Schliesslich nehmen wir an, dass f_0 die Gestalt hat: ²⁾

$$f_0 = \Phi(Ae^{-\beta x}) \quad (32)$$

wo Φ eine willkuerliche Funktion ihres Argumentes ist,

$$\beta = \frac{1}{kT} \quad \text{und} \quad x = \frac{m}{2} (\xi_1^2 + \xi_2^2 + \xi_3^2) = \frac{m}{2} v^2 \quad (33)$$

§ 2. Die lineare Integralgleichung fuer die Verwehungsstörung $g(x, \xi)$.

Der Methode von LORENTZ folgend beachten wir, dass der Bestandtheil f_0 in f keinen Beitrag zu den Stossgliedern auf der rechten Seite von (30) liefert, und vernachlaessigen andererseits die Beitrage von g zur *linken* Seite von (30). (30) geht so ueber in

$$\frac{\partial f_0}{\partial \xi_r} \frac{eF_r}{m} + \frac{\partial f_0}{\partial x_r} \xi_r = \int d\omega' [g(\xi') - g(\xi)] W(xv; a' a) \quad (34)$$

¹⁾ Siehe LORENTZ, l.c. A S. 443, Formel (10); l.c. B S. 342, Formel (10); l.c. C S. 180, Formel (15) und SOMMERFELD, l.c. S. 19, Formel (44).

Wenn man das PAULI-VERBOT beruecksichtigt, d.h. Fermi-Statistik nimmt, tritt eine Komplikation auf. NORDHEIM (On the Kinetic Method in the New Statistics and its Application in the Electron Theory of Conductivity, Proc. R. Soc. 119, 689, 1928) hat gezeigt, dass rechts die erst noch hinzukommenden Glieder sich wieder gerade wegheben. Wuerde man aber auch noch in (30) den Energieaustausch zwischen Elektronen und Ionengitter mit in Rechnung ziehen, so wuerde dieses Wegheben nicht stattfinden. (Siehe F. BLOCH l.c. S. 594, Fussnote). Es ist uns nicht bekannt, ob irgend jemand untersucht hat, ob das PAULI-VERBOT nicht vielleicht auch Komplikationen auf der linken Seite von (30) mit sich bringt!

²⁾ Dies ist sowohl bei LORENTZ [$\varphi(u) = u$] als auch bei SOMMERFELD [$\varphi(u) = \frac{u}{1+u}$]

der Fall. Wenn man aber, wie das BLOCH thut, bei der Quantisierung der Elektronenbewegung das Kraftfeld des Ionengitters mit beruecksichtigt, so ist zwar f_0 stets noch zentrisch symmetrisch im ξ , z Raum, aber nicht mehr kugelsymmetrisch (Siehe z. B. BLOCH, l.c. S. 566, Gl. (28)).

Es ist aber:

$$\frac{\partial f_0}{\partial \xi_r} = \frac{\partial f_0}{\partial x} \cdot m \xi_r \quad \xi_r = v a_r \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Somit erhalten wir fuer g folgende lineare Integralgleichung:

$$a_r v \left(\frac{\partial f_0}{\partial x} e F_r + \frac{\partial f_0}{\partial x_r} \right) = \int d\omega' [g(xv; a') - g(xv; a)] W(xv; a' a) \quad . \quad (36)$$

Setze zur Abkuerzung:

$$v \left(\frac{\partial f_0}{\partial x} e F_r + \frac{\partial f_0}{\partial x_r} \right) = P_r(x, v) \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

(36) geht dann ueber in:

$$a_r P_r(x, v) = \int d\omega' W(xv; a'_1 a'_2 a'_3, a_1 a_2 a_3) [g(x, v; a'_1 a'_2 a'_3) - g(xv; a_1 a_2 a_3)] \quad (39)$$

Betrachte nun die drei einfacheren Integralgleichungen:

$$a_r = \int d\omega' W(x, v; a' a) [G_r(x, v; a'_1 a'_2 a'_3) - G_r(x, v; a_1 a_2 a_3)] \quad (40)$$

($r = 1, 2, 3$)

Denkt man sie sich geloest,¹⁾ so bestimmt sich g aus diesen Loesungen $G_r(x, v; a)$ folgendermassen:

$$g(xv; a_1 a_2 a_3) = P_r(x, v) \cdot G_r(x, v; a_1 a_2 a_3) \quad . \quad . \quad . \quad (41)$$

¹⁾ Fuer den Fall eines voellig isotropen Leitermodells, d.h. wenn in $W(x, v; a'_1 a'_2 a'_3, a_1 a_2 a_3)$ nicht die Richtungen a' und a selber, sondern nur der Winkel zwischen ihnen eine Rolle spielt, hat LORENTZ gezeigt, l.c. A. S. 445, Gl. (17), B. S. 345 Gl. (17) C. S. 186, dass sich die Integralgleichung durch einen sehr einfachen Ansatz elementar loesen laesst.

Da SOMMERFELD ebenfalls mit einem isotropen Modell arbeitet, konnte er das LORENTZsche Loesungsverfahren uebernehmen. l.c. Gl. (43). Ebenso HOUSTON l.c. im ersten Theil seiner Arbeit. l.c. § 2 Gl. (1) (6).

Hingegen scheint uns die Uebertragung dieses Verfahrens auf ein *anisotropes* Leitermodell im zweiten Theil von HOUSTONS Arbeit. — § 8 Gl. (33) — auf einem Versehen zu beruhen und zu einem inneren Widerspruch zu fuehren, so dass wir die dort explizite gegebene Loesung der Integralgleichung fuer unrichtig halten. Man erkennt diesen inneren Widerspruch aus HOUSTONS Gl. (40): Von $\chi(v)$ muss naemlich ausdruuecklich vorausgesetzt werden, dass es *nicht* von der Bewegungsrichtung der Elektronen abhaengt, denn nur dann kann es als (gemeinsamer) Faktor von $f(\xi'_1 \xi'_2 \xi'_3) - f(\xi_1 \xi_2 \xi_3)$ in (6) und (33) vor das Integral gezogen werden. Die Endgleichung (40) widerspricht aber diesem Ausgangspunkt, indem sie besagt, dass $\chi(v)$ ausser von v auch noch von $\alpha_0 \beta_0$ abhaengt. — An einem zweidimensionalen Modell kann man sich deutlich machen, dass im Fall von *Anisotropie* nur fuer eine spezielle, kuenstliche Form von $W(a', a)$ das LORENTZsche Verfahren zur Loesung der Integralgleichung (nach sinnemaesser Verallgemeinerung) anwendbar bleibt. Diese Ausfuehrungen moegen rechtfertigen, warum wir hier nicht versucht haben, die Loesung der Integralgleichung mehr explizite zu geben.

§ 3. Bestimmung des elektrischen Stromes und Energiestromes aus g .
Die Komponenten der elektrischen Stromdichte sind:

$$i_s(x_1, x_2, x_3) = e \iiint d\xi_1 d\xi_2 d\xi_3 g(x_1, x_2, x_3, \xi_1, \xi_2, \xi_3) \cdot \xi_s \quad (42)$$

Die der Energiestromdichte:

$$W_s(x_1, x_2, x_3) = \int d\tau \cdot g \cdot \frac{mv^2}{2} \xi_s \quad (43)$$

Fuehre fuer diese Integrationen im $\xi_1 \xi_2 \xi_3$ Raum Polarkoordinaten mit Volum-element

$$v^2 dv d\omega$$

ein, so gehen (42), (43) ueber in:

$$i_s(x) = \int_0^\infty dv v^2 e P_r(xv) \cdot v \int d\omega G_r(xv; a_1 a_2 a_3) \cdot a_s \quad (44)$$

$$W_s(x) = \int_0^\infty dv v^2 \frac{mv^2}{2} P_r(xv) \cdot v \int d\omega G_r(xv; a_1 a_2 a_3) \cdot a_s \quad (45)$$

oder unter Einfuehrung der Bezeichnung

$$\int d\omega G_r(xv; a_1 a_2 a_3) \cdot a_s = \Gamma_{rs}(x, v) \quad (46)$$

$$i_s = \int_0^\infty dv \cdot v^4 \cdot e \left[\frac{\partial f_0}{\partial x} e F_r + \frac{\partial f_0}{\partial x_r} \right] \Gamma_{rs} \quad (47)$$

$$W_s = \int_0^\infty dv v^6 \frac{m}{2} \left[\frac{\partial f_0}{\partial x} e F_r + \frac{\partial f_0}{\partial x_r} \right] \Gamma_{rs} \quad (48)$$

Setze zur Verkuerzung:

$$e \int dv v^4 \frac{\partial f_0}{\partial x} \Gamma_{rs}(xv) = A_{rs}(x) \quad (49)$$

$$e \int dv v^4 \frac{\partial f_0}{\partial x_r} \Gamma_{rs}(xv) = B_s(x) \quad (50)$$

$$\frac{m}{2} \int dv v^6 \frac{\partial f_0}{\partial x} \Gamma_{rs}(xv) = C_{rs}(x) \quad (51)$$

$$\frac{m}{2} \int dv v^6 \frac{\partial f_0}{\partial x_r} \Gamma_{rs}(x, v) = D_s(x) \quad (52)$$

Dann wird:

$$i_s = A_{rs} e F_r + B_s \quad (53)$$

$$W_k = C_{lk} e F_r + D_k \quad (54)$$

§ 4. Die Tensoren $\Gamma_{rs}(xv)$, $A_{rs}(x)$, $C_{rs}(x)$ sind symmetrisch. Zum Beweis multipliziere die Integralgleichung (40) fuer G_r mit $G_s(a)$ und integriere ueber $d\omega$

$$\int d\omega a_r G_s(a_1 a_2 a_3) = \int d\omega \int d\omega' W(a'a) G_r(a') G_s(a) - \int d\omega G_r(a) G_s(a) \int d\omega' W(a', a) \quad (55)$$

Wegen der Symmetrie von $W(a'a)$ (Gl. (29)) ist das erste Doppelintegral rechts symmetrisch in r und s und damit die ganze rechte Seite.

Das Integral links ist — Gl. (46) — Γ_{rs} , womit dessen Symmetrie bewiesen ist. Diese Symmetrie uerbetraegt sich — Gl. (49, 51) — auf $A_{rs}(x)$ und $C_{rs}(x)$.

Bemerkung: Fuer den zu A_{rs} reziproken Tensor a_{rs} gilt wegen

$$a_{qs} A_{rs} = \delta_{qr} \quad (56) \quad \text{ebenfalls:} \quad a_{qs} = a_{sq} \quad (57)$$

§ 5. Berechnung der reversibelen Waermeentwicklung $\omega(x_1 x_2 x_3)$. Die totale Waermeentwicklung $\Omega(x_1 x_2 x_3)$ per Volumen- und Zeiteinheit ist gegeben durch:¹⁾

$$\Omega = F_q i_q - \frac{\partial W_p}{\partial x_p} \quad (58)$$

In der That: Das erste Glied bedeutet die sekundliche Arbeitszufuhr an die in der Volumeneinheit befindlichen Elektronen; das zweite den sekundlichen Energiezuwachs der Volumeneinheit wegen der Aufstauung des W -Stromes. Bei Stationaritaet muessen dann die Metallatome den Elektronen gelegentlich der Zusammenstoesse diesen Energieueberschuss fortwaehrend abnehmen.²⁾

Aufloesung der Gl. (53) nach F gibt:

$$eF_q = a_{qs} i_s - a_{qs} B_s \quad (59) \quad \text{wo} \quad a_{qs} A_{rs} = \delta_{qr} \quad (60)$$

Einsetzen von (59) in (58) und (54) liefert:

$$\Omega = F_q i_q - \frac{\partial W_p}{\partial x_p} = i_s i_q \frac{a_{qs}}{e} - i_q a_{qs} \frac{B_s}{e} - \frac{\partial}{\partial x_p} (i_s a_{qs} C_{qp}) - \frac{\partial}{\partial x_p} (-B_s a_{qs} C_{qp} + D_p) \quad (61)$$

Das erste Glied rechts ist die Joule-Waerme, das letzte die von der

¹⁾ Vergl. z.B. LORENTZ, l.c. A. S. 587, Gl. (37); B. S. 355, § 12; SOMMERFELD, l.c. S. 43, Gl. (58).

²⁾ Den Darstellungen von LORENTZ, SOMMERFELD und HOUSTON folgend, haben wir in den Gl. (30) den Einfluss des Energieaustausches mit dem Ionengitter nicht explizite in Rechnung gebracht. Wie das zu geschehen hat findet man bei BOHR l.c. § 2 Gl. (10) u. (14) — fuer klassische Statistik — und bei BLOCH l.c. § 5 — fuer Quanten-Statistik.

irreversibelen Waermeleitung herruehrende Waermeentwicklung. Der reversible Theil der Waermeentwicklung (dem Strom proportional) ist:

$$\omega = - \frac{\partial}{\partial x_p} (i_s a_{qs} C_{qp}) - i_q a_{qs} \frac{B_s}{e} \quad . \quad . \quad . \quad (62)$$

Wir haben sogleich den Ausdruck $\frac{\omega}{T} = k \vartheta \omega$ noethig. Es ist:

$$\left. \begin{aligned} \vartheta \omega &= - \frac{\partial}{\partial x_p} (i_s a_{qs} C_{qp} \vartheta) + i_s a_{qs} C_{qp} \frac{\partial \vartheta}{\partial x_p} - i_q a_{qs} \frac{B_s}{e} \vartheta = \\ &= - \frac{\partial}{\partial x_p} (i_s a_{qs} C_{qp} \vartheta) + M \end{aligned} \right\} \quad (63)$$

§ 6. *Einfuehrung der Annahme* $f_0(x_1 x_2 x_3) = \Phi(A e^{-\vartheta \kappa})$.

Es wird dann:

$$\frac{\partial f_0}{\partial x} = - \vartheta \cdot \varphi(x_1 x_2 x_3, v) \quad . \quad . \quad . \quad (64)$$

$$\frac{\partial f_0}{\partial x_r} = \left(\frac{\partial \lg A}{\partial x_r} - \kappa \frac{\partial \vartheta}{\partial x_r} \right) \cdot \varphi(x, v) \quad . \quad . \quad . \quad (65)$$

wo zur Abkuerzung gesetzt ist:

$$\Phi'(A e^{-\vartheta \kappa}) \cdot A e^{-\vartheta \kappa} = \varphi(x_1 x_2 x_3, v) \quad . \quad . \quad . \quad (66)$$

Die Gleichungen (49—52) liefern dann (beachte auch dass $\kappa = \frac{mv^2}{2}$):

$$A_{ab} = - e \vartheta IV_{ab} \quad . \quad . \quad . \quad (67)$$

$$\frac{1}{e} B_d = \frac{\partial \lg A}{\partial x_c} IV_{cd} - \frac{m}{2} VI_{cd} \frac{\partial \vartheta}{\partial x_c} \quad . \quad . \quad . \quad (68)$$

$$C_{ef} = - \frac{m}{2} \vartheta VI_{ef} \quad . \quad . \quad . \quad (69)$$

$$D_h = \frac{m}{2} \left[\frac{\partial \lg A}{\partial x_g} VI_{gh} - \frac{m}{2} VIII_{gh} \frac{\partial \vartheta}{\partial x_g} \right] \quad . \quad . \quad . \quad (70)$$

falls man zur Abkuerzung setzt:

$$\int dv \cdot v^n \varphi(xv) \Gamma_{rs}(x, v) = IV_{rs}(x), \quad VI_{rs}(x), \quad VIII_{rs}(x) \quad \left(\begin{array}{l} \text{fuer } n=4, 6, 8 \end{array} \right) \quad (71)$$

Wir bemerken noch, dass aus (60) und (67) folgt:

$$a_{qs} \cdot IV_{ps} = - \frac{1}{e \vartheta} \delta_{pq} \quad . \quad . \quad . \quad (72)$$

§ 7. Man gelangt zu KELVIN's Gleichung (I) fuer ω .

Der Term M in (63) kann naemlich folgendermassen transformiert werden:

$$M = -i_q a_{qs} \frac{B_s}{e} \vartheta + i_s a_{qs} C_{qp} \frac{\partial \vartheta}{\partial x_p} = -i_q a_{qs} IV_{ps} \frac{\partial \lg A}{\partial x_p} \vartheta + \left. \begin{aligned} &+ i_s a_{qs} \frac{m}{2} VI_{sp} \frac{\partial \vartheta}{\partial x_p} \vartheta - i_s a_{qs} \frac{m}{2} \vartheta VI_{qp} \frac{\partial \vartheta}{\partial x_p} \end{aligned} \right\} \quad (73)$$

Vertausche im zweiten Term die Summationsindices (s, q) miteinander, dann vereinigt er sich mit dem dritten zu

$$\frac{m}{2} \vartheta i_s \frac{\partial \vartheta}{\partial x_p} VI_{qp} [a_{sq} - a_{qs}] = 0 \quad \dots \quad (74)$$

(wegen (57)).

Der erste Term und damit M ueberhaupt vereinfacht sich weiter wegen (72) zu

$$M = \delta_{qp} \frac{i_q}{e} \frac{\partial \lg A}{\partial x_p} \quad \dots \quad (75)$$

aber wegen Divergenzfreiheit des Stromes ist

$$\frac{\partial}{\partial x_p} (\delta_{qp} i_q) = \frac{\partial i_p}{\partial x_p} = 0 \quad \dots \quad (76)$$

und deshalb M auf reine Divergenzform zu bringen:

$$M = \frac{\partial}{\partial x_p} \left(\delta_{qp} \frac{i_q}{e} \lg A \right) \quad \dots \quad (77)$$

Dank (77) gewinnt man nun unmittelbar aus (63, 69) KELVIN's Gleichung (I):

$$\frac{\omega(x_1 x_2 x_3)}{T} = k \vartheta \omega = \frac{\partial}{\partial x_p} (i_s S_{sp}) \quad \dots \quad (I)$$

mit folgender kinetischen Auswertung des Tensors

$$\frac{1}{k} S_{sp} = \delta_{sp} \frac{1}{e} \lg A + \frac{m}{2} \vartheta^2 a_{qs} VI_{qp} \quad \dots \quad (78)$$

Bemerkungen. 1. Dass der BRIDGMANEffekt und $\Pi_{\perp \parallel}$ wesentlich verknuepft sind mit der (anisotropen) Abhaengigkeit der Elektronenbeweglichkeit von ihrer Geschwindigkeit sieht man folgendermassen:

Falls in (28) die Uebergangswahrscheinlichkeit $W(xv; a'_1 a'_2 a'_3, a_1 a_2 a_3)$ von v unabhaengig ist, (also auch Unabhaengigkeit der mittleren Weglaenge eines Elektrons von seiner Geschwindigkeit v), so ist in (40) auch G_r und also — siehe (46) — Γ_{rs} unabhaengig von v . Letztere Groesse laesst sich dann in (49) und (51) vor das Integral ziehen, so dass alle Komponenten des Tensors C_{rs} den entsprechenden von A_{rs} proportional werden. Das gleiche gilt dann wegen (67) und (69) von den beiden

Tensoren VI_{rs} und IV_{rs} ; somit liefert (72) bei Ersetzung von IV_{ps} durch VI_{ps} -abgesehen von Aenderung des skalaren Faktors- wieder δ_{qp} und — siehe (78) — der KELVINSche Tensor S_{sp} erhaelt die *isotrope Form* $\delta_{sp} S(x)$. Dann aber verschwindet in der That der BRIDGMAN-effekt und die verwandten Effekte, wie schon I § 2A gezeigt wurde.

2. Trotz der Symmetrie der Tensoren α_{qs} und VI_{qp} (siehe § 4) wird im Allgemeinen $\alpha_{qs} VI_{qp} \neq \alpha_{qp} VI_{qs}$ sein, also $S_{sp} \neq S_{ps}$ (vergl. I § 8) worauf schon KELVIN in seiner thermodynamischen Ueberlegung sehr ausfuehrlich hinwies.¹⁾

§ 8. KELVIN's Gleichungen (II) fuer die electromotorischen Kraefte gewinnt man durch Transformation des Termes F_s auf die Gestalt:

$$F_s = \frac{i_q}{e} a_{sq} - \frac{B_q}{e} a_{sq} = F_s^i + F_s^x, \quad . \quad . \quad . \quad (79)$$

(vergl. (59))

$$F_s^x = -\frac{B_q}{e} a_{sq} = -\frac{\partial \lg A}{\partial x_p} IV_{pq} a_{sq} + \frac{m}{2} VI_{pq} a_{sq} \frac{\partial \vartheta}{\partial x_p} \quad . \quad . \quad (80)$$

Der erste Term rechts ist wegen (60) gleich

$$\frac{\partial \lg A}{\partial x_p} \frac{\delta_{ps}}{e \vartheta} = \frac{\partial}{\partial x_p} \left(\frac{\delta_{ps}}{e \vartheta} \lg A \right) - \frac{\delta_{ps}}{e} \lg A \frac{\partial}{\partial x_p} \left(\frac{1}{\vartheta} \right) \quad . \quad . \quad (81)$$

Somit:

$$F_s^x = \frac{\partial}{\partial x_s} \left(\frac{1}{e \vartheta} \lg A \right) + \left[\delta_{ps} \frac{1}{e \vartheta^2} \lg A + \frac{m}{2} VI_{pq} a_{sq} \right] \frac{\partial \vartheta}{\partial x_p} \quad . \quad (82)$$

Setze

$$\frac{1}{e \vartheta} \lg A = R \quad . \quad . \quad . \quad . \quad . \quad . \quad (83)$$

beachte, dass (§ 4) $VI_{pq} = VI_{qp}$, $a_{sq} = a_{qs}$ und vergleiche (78), so ergibt sich

$$F_s^x = \frac{\partial R}{\partial x_s} + \frac{1}{k \vartheta^2} \frac{\partial \vartheta}{\partial x_p} S_{sp} = \frac{\partial R}{\partial x_s} - S_{sp} \frac{\partial T}{\partial x_p} \quad . \quad . \quad . \quad (84)$$

Die physikalische Bedeutung von F_s^i und F_s^x gewinnt man aus (79) durch folgende Bemerkungen:

$$E_s^i = -\frac{i_q}{e} a_{sq} \quad . \quad . \quad . \quad . \quad . \quad . \quad (85)$$

ist die vom Ohmschen Widerstand herruehrende elektromotorische Kraft des Leiterelementes, also

$$e F_s^i = -e E_s^i \quad . \quad . \quad . \quad . \quad . \quad . \quad (86)$$

derjenige Theil der gesammten, die Elektronen (zwischen den Zusammen-

¹⁾ W. THOMSON, Math. and Phys. Papers I (1882). S. 275, § 158.

stoessen) beschleunigenden Kraft eF_s , der zur *Ueberwindung* von E_s^i noetig ist. — Analog ist in (79)

$$eF_s^x = -eE_s^x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (87)$$

derjenige Bestandtheil, der zur *Ueberwindung* der elektromotorischen Kraft

$$E_s^x = \frac{B_q}{\mathfrak{E}} a_{sq} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

noetig ist. Das ist also diejenige elektromotorische Kraft des Leiter-
elementes, die auch noch bei verschwindendem i wegen der Inhomoge-
nitaet und ungleichen Erwaermung des Materials bestehen bleibt. Wegen
(87) nimmt also (84) die Form von KELVIN's Gl (II) an:

$$E_s^x = S_{sp} \frac{\partial T}{\partial x_p} - \frac{\partial R}{\partial x_s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

Damit ist die *kinetische* Interpretation der Relationen vollzogen, die
im Theil I *thermodynamisch* behandelt worden waren.

Anatomy. — *Preface to Volume II of the microscopical atlas of the human brain.* By C. WINKLER.

(Communicated at the meeting of September 28, 1929).

At Frankfurt am Main, during the meeting of the so-called Brain-commission (a commission for brain-research founded by the international Association of the Academies) a discussion took place in May 1912, after a proposition brought forward by Prof. W. WALDEYER of Berlin and by Prof. L. EDINGER of Frankfurt am Main.

They proposed to continue the admirable technical work, done, now more than 60 years ago by Dr. BERNARD STILLING, in drawing a macroscopical atlas of the human brain. They wanted the production of a new atlas, but now a microscopical one, made in an enlargement of forty times, because the better knowledge of the brain-tissue and the more evident details of the different fibre-systems and cell-groups contained in it, were asking for a renewal of STILLING's work.

Their proposition was warmly defended by Prof. C. VON MONAKOW of Zürich and by myself, but it did not seem so easy to prepare the publication of such an atlas. At first there must be made a standard-series of uninterrupted sections through the human brainstem. In order to have a very simple one, the brainstem of a normal child was chosen, not older than one year of age. This seemed to be a specimen of a brainstem with most simplified, not yet all medullated systems of fibres, less complicated than that of the adult man.

The commission accepted, that after fixation of such a brain in chromic salts, and embedding in celloidine, the sections should be made in a frontal direction, perpendicular to the longitudinal axis of the medulla oblongata, as was first proposed and done by MEYNERT. This series, in the so-called direction of MEYNERT, should be stained after the WEIGERT—PAL-method and with Carminas-Ammoniae.

I promised to make such a series. Dr. JOSSELIN DE JONG of Rotterdam, now Professor of pathological anatomy at the University of Utrecht, provided me with the brains of a normal child, aged one year, and dead of scarlatina.

The brain was taken out a few hours after death, hardened and embedded, and an uninterrupted series of sections was made in the direction as mentioned above. The series began at the second cervical segment and ended at the commissura cerebri anterior. It remained at the disposal of the Brain-commission and the medulla oblongata was sent to the Brain-institute

of Zürich, because Prof. VON MONAKOW had accepted the task to produce, in the laboratory of the Brain-institute of Zürich, six drawings of sections through the medulla oblongata.

In the laboratory of Amsterdam should be made the six following drawings through the entrance of the medulla oblongata in the pons of VAROLI and through the distal end of the latter, by Dr. ADA POTTER and by myself.

The first conception of the new atlas began in this way.

Moreover six other drawings were to be made of the middle of the pons, including the origin of the Nervus trigeminus, of its upper end and the caudal end of the mesencephalon. The six following drawings of sections were projected through the pedunculus cerebri and the hypothalamus, whereas the last six drawings were to be made from sections through the basal ganglia as far as the commissura cerebri anterior. The total project of the atlas, thus contained thirty drawings in MEYNERT's direction through the same brain of a normal child of one year, from sections magnified forty times, after staining by WEIGERT—PAL's method and with a cell-staining, controlled by the members of the Brain-institute and made by competent men. It was to become a standard-atlas for the use of medical men, interested in Neurology or Psychiatry.

Afterwards the atlas was to be completed by additionnal plates. Details of special parts of the nervous system, as f.i. the corpus geniculatum laterale, the nuclei thalami optici, the details of the fillet might be given therein, as well as drawings of sections in other directions through the brain.

Prof. VON MONAKOW found in Dr. FUSE, now Prof. of anatomy at the University of Sendai in Japan, not only an artist, but also an expert in the anatomy of the brain, a man able to draw the sections through the medulla oblongata. The first volume of the new atlas "the medulla oblongata" appeared in 1916.

The artistic plates drawn by Dr. FUSE were printed by the care of the ORELL-FÜSSLI-Institute of Zürich and were accompanied by an introduction by Prof. VON MONAKOW.

Dr. ADA POTTER and I began the drawing of the second volume of the atlas, the part of the nervous system where the frontal end of the medulla oblongata enters into the pons of VAROLI.

Now, however many difficulties arose.

The war was the cause of financial obstacles, opposing themselves to the printing of the second volume, that had been drawn in Holland. They were so many that the publication of the second volume of the atlas was postponed from year to year. At the moment when the "Koninklijke Akademie van Wetenschappen" was able to give a solution to the financial difficulties, in 1929, the second volume of the atlas was published.

But further difficulties arose from the fact that scientific men, drawing sections of the nervous system, differ so much from one another in their conception of the drawn specimen, that it was nearly impossible to

understand, how they could make such wholly different drawings of neighbouring slides from the same series.

The drawings of Dr. FUSE, of Dr. ADA POTTER and those made by myself, differed so much, that they could hardly be compared with each other. Therefore the first and the second volumes of the atlas cannot have the same standing. The two volumes represent quite different conceptions of the nervous system.

And, finally, a most annoying difficulty presented itself: it became clear, that it would not be possible to maintain an enlargement of forty times, adopted in the first volume, in drawings of the pons VAROLI, of the pedunculus cerebri and of the basal ganglia.

A diameter of 3 cm. in any direction of a section, would call for a drawing of 120 cm., a dimension much too large for the practical use of an atlas.

And yet, if a smaller scale were adopted, firstly the drawings from sections of the pons VAROLI, made on a smaller scale could no longer be compared with those made from sections of the medulla oblongata, and secondly it appeared that on a smaller scale, the details of many fibre-systems in the tegmentum pontis, were not quite so distinctly visible as they should have been.

If the Brain-commission had still existed, there would have been a new discussion in order to know whether it was desirable to have a total aspect in the drawings of sections through the pons, the pedunculus cerebri and the basal ganglia, with, if necessary, additional drawings on a much larger scale, or whether the total aspect of the sections should be given up, and different parts of given section be treated separately, e.g. between the ventral part of the pons and its tegmentum.

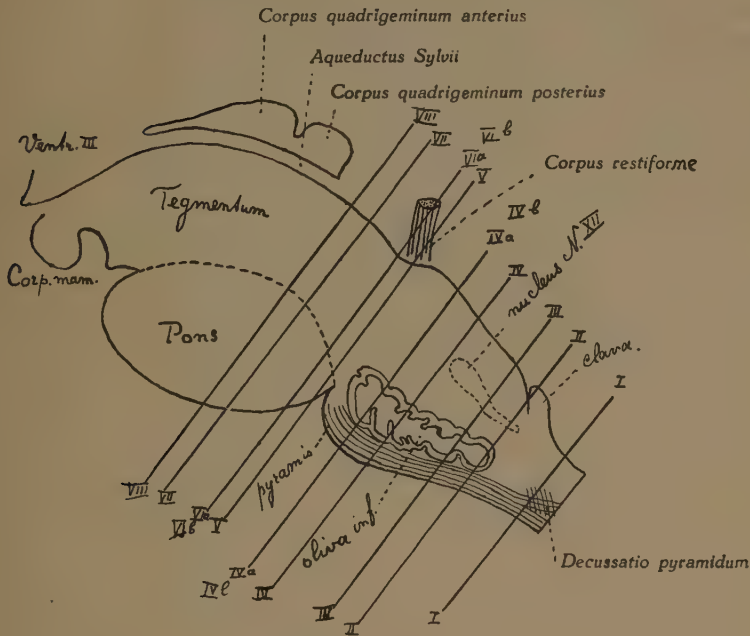
But now, since the "Koninklijke Akademie van Wetenschappen" has solved the financial difficulties, and the second volume has been published, a few words may be said regarding the details of this volume.

The same scheme, which was followed in the first volume by Prof. VON MONAKOW, has been adhered to in the second volume. The drawings given therein are the numbers IVa, IVb, VIa, VIb, VII and VIII of the scheme, corresponding to the numbers N^o. 330, 328, 410, 406, 430, 442, of the series. They indicate the levels of the drawings, of which Tabula IVa and VIa were made by myself, and IVb, VIb, VII and VIII by Dr. ADA POTTER.

The cell-preparations were drawn after very good cell-preparations stained with carminas ammoniae, not after NISSL's method, because it seemed an advantage to use the same series of the WEIGERT-PAL preparations, which could not, at that time be used for the NISSL-method, as that staining was not yet possible in objects hardened in chromic salts.

We must say a few words on the nomenclature followed in this volume. As nearly as possible, we have followed the same nomenclature as used by VON MONAKOW and FUSE. A few changes were however necessary. In Germany the inner part of the corpus restiforme is described by MEYNERT

as the "innere Abtheilung des unteren Kleinhirn-Stieles" and VON MONAKOW has therefore called this part I. A. K. But in other countries



SCHEMA SAGITTALE

sectionum pedunculi cerebri transmissum in planum unum.
 Lineae I, II, III, IV, V indicant tabulas Monakowi Fuseique.
 Tabula IVa (N^o. 330) Tabula IVb (N^o. 328)
 Tabula VIa (N^o. 410) Tabula VIb (N^o. 406)
 Tabula VII (N^o. 430) Tabula VIII (N^o. 442)

the name "corpus juxta-restiforme" is used for this part of the corpus restiforme. In the drawings of this volume both names will be found.

As to the central bundle of the tegmentum pontis a difficulty arose, in its being a very badly defined tract. It is formed by a great number of fibres of different origin and ending.

A ventral part of it is seen as a solid fibre-mass of fine fibres packed together, without any grey reticula between their bundles. This contrifugal fibre-system receives its fibres, partly from the nucleus pallidus, partly from the red nucleus and finds its ending in the fibre-mantle of the nucleus olivaris inferior. This part of the tractus centralis tegmenti is called the tractus pallido-rubro-olivaris.

A more dorsal part of the central tract of the tegmentum, is formed by bundles of fibres, separated by small reticula of grey matter. Among

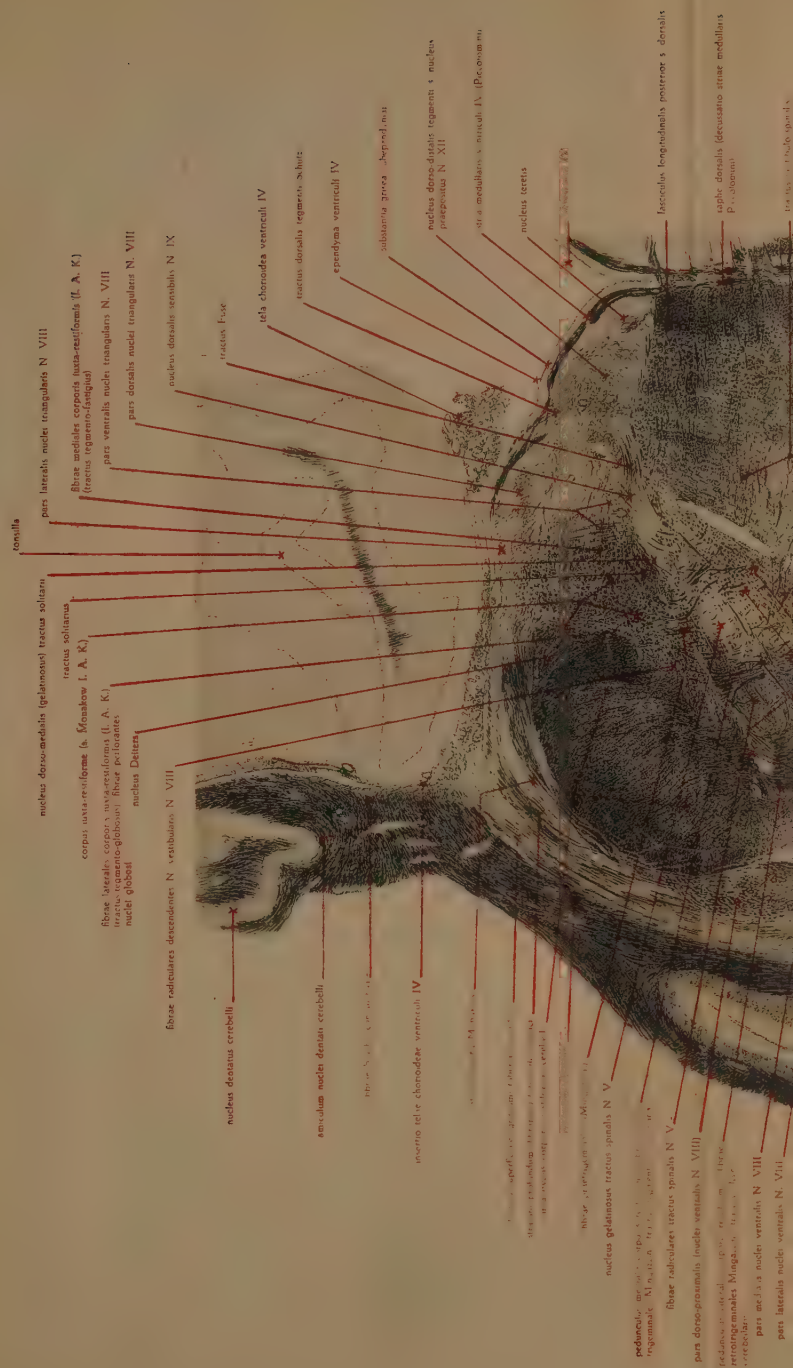
those fibres are also centrifugal fibres, issuing from the nucleus pallidus and the red nucleus, but their ending is found partly in the grey reticula separating the bundles, partly in the formatio reticularis temmenti of the medulla oblonata and even of the medulla spinalis. That part of the tractus centralis tegmenti is called : "the tractus pallido-rubro-reticularis".

Besides these, there enter into the tractus centralis tegmenti a great many of centripetal fibres, from the grey reticula and from the formatio reticularis, toward the nucleus pallidus and the red nucleus. These centripetal fibres join the two centrifugal fibre-systems, and it is not very easy to distinguish the centripetal system from the others.

In all drawings three bundles may be distinguished, a tractus pallido-rubro-olivaris, a tractus pallido-rubro-reticularis and a rest which is called the tractus centralis tegmenti. Together they build up the tractus centralis tegmenti of the anatomical books.

It certainly would be valuable, if a reconstructed Brain-commission were to reconsider the plan of the publication of the entire brain. This, however, will be the task of younger persons.

C. WINKLER: PREFACE TO VOLUME II OF THE MICROSCOPICAL ATLAS OF THE HUMAN BRAIN.





C. WINKLER: PREFACE TO VOLUME II OF THE MICROSCOPICAL ATLAS OF THE HUMAN BRAIN.

corpus ovata residuum cerebelli (Monakow I A K)

fibrae laterales corporis ovatae residuum (I A K)

tractus tegmento-globosus, fibrae perforantes nucleos globosos

fibrae radiales descendentes N vestibularis N VIII

N vestibularis N VIII

brachium pedunculi cerebelli

area callosa, corpus trilaterale cerebelli

fibrae ucliales corporis ovatae-residuum (I A K)

tractus tegmento-globosus

operculum ventriculi IV

nucleus Duxeri

nucleus triangulatus N. VIII

tractus solitarius (polus dorsalis)

nucleus foveae-medialis (gelatinosus) tractus solitarius (pars dorsalis nucle)

tractus vestibulo-aqualis

substantia grisea subependymalis ventriculi IV

fibrae radiales N. VII

nucleus N. abducens (pars dorsalis)

tractus dorsalis segmenti Schütz

genu N. facialis (pars anterior)

nucleus praepontinus N. XII

ventriculus IV

nucleus tertius

fibrae dorsales ad raphem

e stria acutica Monakow

tractus vestibulo-spinalis

fasciculus longitudinalis posterior s. dorsalis

raphe dorsalis

tractus secundarius dorsalis N. V

fibrae concomitantes nucle N. V

fasciculus praedorsalis

pars dorsalis nucle N. VII

fasciculus parafascialis ascendens

pars ventro-lateralis nucle N. VII

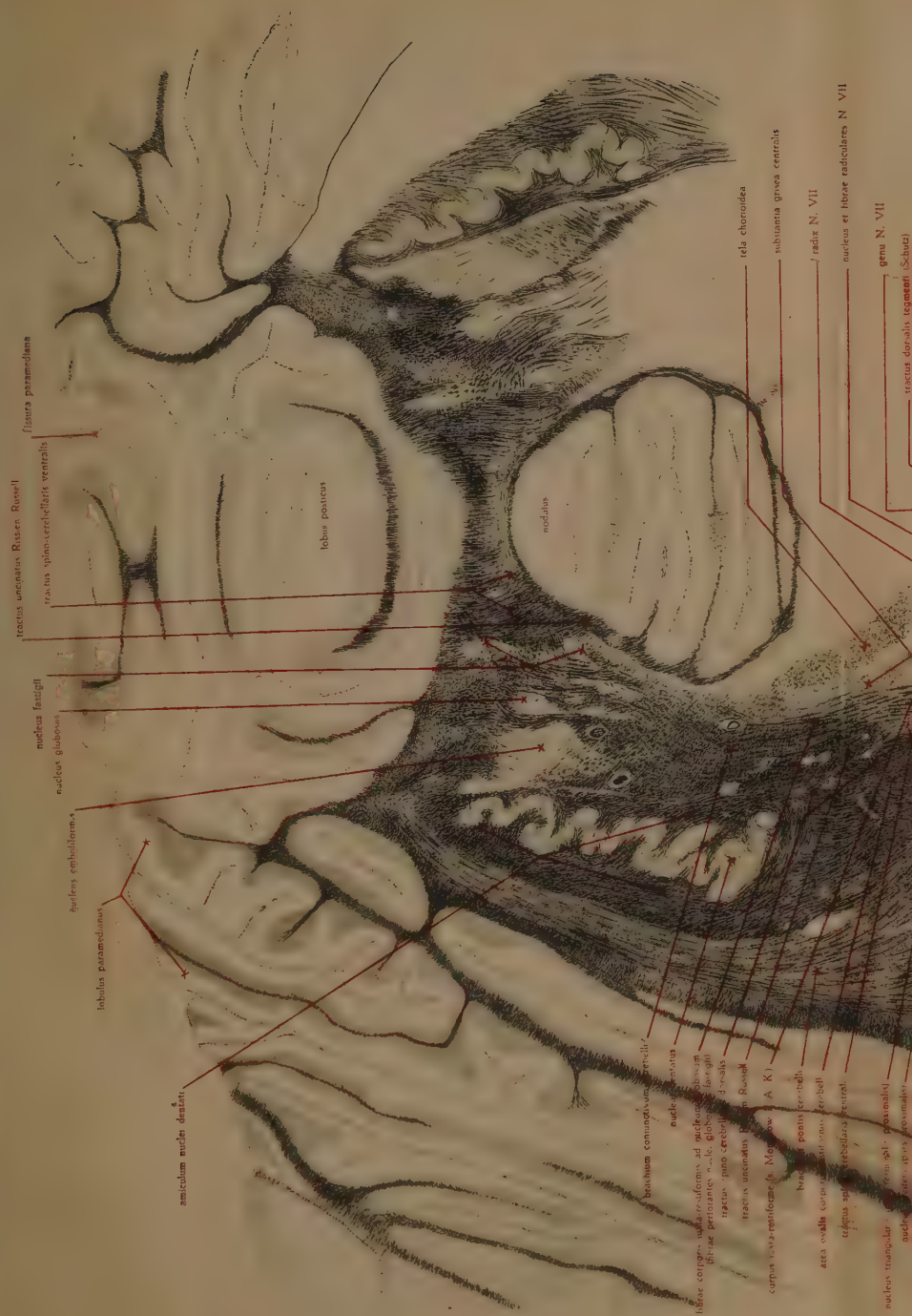
raphe medialis

pars ventro-medialis nucle N. VII

tractus centralis segmenti

nucleus olivaris superior

nucleus reticularis medio-ventralis (Bichteraw)



nucleus globosus
libere perforans nucleu globosi
nucleus fastigi

lobulus paramedianus
fossa paramediana

lobus posterior a. culum vermis

nucleus emboliformis

nucleus dentatus

anellum nucleu dentati

brachium posterius cerebelli

brachium superiorum cerebelli

tractus anterior. Raven Russell

corpus restiforme cerebelli

tractus spinocerebellaris ventralis

tractus spinocerebellaris ventralis

tractus anterior. Raven Russell

illae corporis ista restiformis
(Monakow I. A. K) ad
nucleum globosum

ola choroides ventricul. IV

nucleus medio ventralis brachii connectivum

substantia grisea cerebelli

tractus vestibulo-mesencephalicus

area acustica Monakow

status digitalis signatus. Schott

ventriculus IV

Physiology. — *Experimental contributions to the knowledge concerning the segmental innervation of the abdominal muscles in the dog.* (3rd communication). *The M. obliquus internus, the M. transversus abdominis and conclusions.* By Prof. G. VAN RIJNBERK and Miss L. KAISER.

(Communicated at the meeting of September 28, 1929).

Anatomical introduction.

Gross Anatomy. The obliquus internus muscle as well as the M. transversus consists in dog in very thin and broad layers of muscle substance. The obliquus internus is inserted craniad into the last rib and usually also into the cartilage of the last rib but one; medial into an aponeurosis that continues into the sheath of the rectus abdominis, lateral into the dorsolumbal fascia, and caudad into an aponeurosis inserting into the pubic and iliac bone. The fibres run from dorsocranial towards caudoventral. The M. transversus arises craniad from the inner surface of the false ribs, making some connections with the diaaphragm, medial from the sheath of the rectus muscle (linea alba), lateral from the transvers process of the lumbar vertebrae, a fascia intervening, and approaching caudally the pelvis. The fibres take a purely lateromedial course. Neither of the muscles shows any fibrous septa.

Peripheral innervation. The obliquus internus muscle receives its innervation from the medial rami of the lowest thoracic nerves and from the highest lumbar nerves (ileo-hypogastric and ileo-inguinal).

The transversus muscle receives its innervation from the same nerves. The peripheral segmental nerve branches that provide the motor innervation of the rectus muscle are six or seven in number and run parallel to the fibres of the transversus on the outer surface of that muscle.

Experimental part.

M. obliquus internus. The data as set forth in this communication were obtained for the obliquus internus muscle from four dogs (D. 9, 11, 49 and 50) and for the M. transversus also from four dogs (D. 11, 29, 49, 50). Method and technique were the same as described in the preceding communications.

Stimulation of one of the ventral medullar roots that takes part in the innervation of the muscle always results in contraction of a definite and circumscribed part of the muscle. The contraction includes a number of fibres

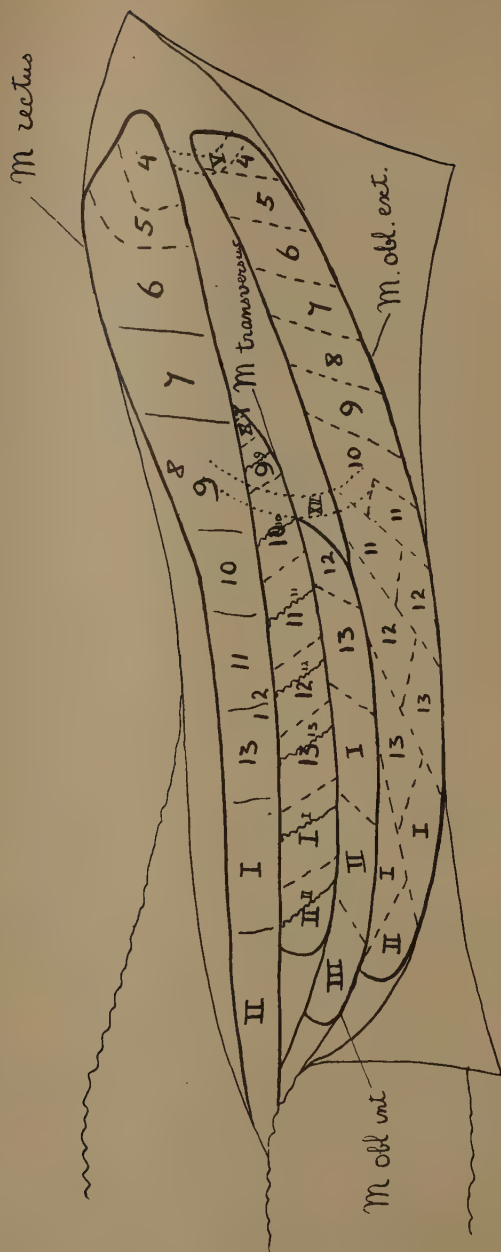


Fig. 1.

Diagram showing the rhizomeres of the four abdominal muscles in dog. The M. obliquus externus is reflected.
4-13 thoracic nerves, I, II, III lumbar nerves, V, XII, ribs.

situated side by side that form a coherent strip of muscle. The contraction may be noted by sight (shortening and change of colour, the fibres turn a darker red) and by feeling (they become firmer). When several roots are stimulated consecutively, the contracted strip can be seen to change its position.

The most cranial root partaking in the innervation of the *M. obliquus internus* is Th 12 (Dog 9 and 50). In one dog (49) the most cranial root was Th 11. But this dog had only twelve ribs. In three cases we found the most caudal root to partake in the innervation L III (Dog 9, 11, 50). In dog 49 with twelve ribs we found also the most caudal root to be L III. The *M. obliquus internus* therefore is innervated by five consecutive spinal segments, Th 12—L III. The anatomical publications do not record L III as partaking in the innervation of the obliquus internus muscle. Even with careful observation there was no reason to assume the occurrence of overlapping in cranio-caudal direction.

M. transversus abdominis. Here also stimulation of roots partaking in the innervation of this muscle resulted in contraction in well-defined territories, situated side by side in cranio-caudal direction.

The most cranial root partaking in the innervation is Th 8 (Dog 11, 50). In dog 49 (that had only twelve ribs) and in dog 29, Th 7 innervated a very small part of the muscle, situated quite cranially. The most caudal root was always L II; in dog 49 L III.

The transversus muscle therefore consists of eight rhizomeres. Those are strictly separated, without any overlapping. Each rhizomere contains a strip of muscle in the middle of which runs the segmental homologous peripheral nerve branch of the rectus and transversus muscle, except in the most cranial strip that does not contain a nerve branch for the rectus muscle. Those segmental nerve branches therefore are situated in regard to the rhizomeres of the transversus muscle intrasegmental, and not intersegmental.

Summary.

1. The *M. obliquus internus* in dog is innervated by an uninterrupted series of five ventral spinal roots: Th 12—L III.

The *M. transversus* is innervated by an uninterrupted series of 8 (?) ventral spinal roots: Th (7) 8—L II.

2. Neither of the muscles shows any segmentation by fibrous septa. The rhizomeres that build up the muscles appear as simple muscle strips laying side by side and forming an uninterrupted series in cranio-caudal direction.

3. Neither muscle shows any trace of mutual overlapping.

4. The peripheral segmental nerve branches that innervate the *M. rectus* and *M. transversus* are situated intrasegmental, not intersegmental, i.e. they are situated in the metameric homologous rhizomere of the transversus muscle.

Conclusion.

Examining the results of our investigation it will be clear that the innervation of the four muscles of the abdominal wall has preserved the original segmental characteristic. The muscle territories that receive their innervation from the various spinal ventral roots (rhizomeres) are situated one after the other in cranio-caudal direction. Those conditions are clearest and most definite in the *M. transversus* and *M. obliquus internus abdominis*, in which the rhizomeres appear without any overlapping, mixing or shifting as a series of well-defined muscle territories (Fig. 1).

In the *M. obliquus externus* there exists the curious condition, that some rhizomeres are divided into two parts: a medial and a lateral division, the two parts having shifted their positions in regard to each other, resulting in a separation of the territories of one rhizomere.

Finally, the *M. rectus abdominis* shows the most important complications. This muscle does not consist of an uninterrupted series of consecutive and well-defined radical territories: one of the ventral roots of the series (Th 8) often does not or only slightly partake in the innervation of this muscle, and mixing and overlapping of rhizomeric material in various segmental levels will occur. This fact is the more remarkable since the *M. rectus abdominis* is the only muscle of the abdominal wall that is divided in apparently segmental territories by fibrous septa.

The serial division of the muscle that is caused in this way however is only metameric with a certain restriction.

Pathology. — *Experimental malaria with protracted incubation.* By
W. A. P. SCHÜFFNER, P. C. KORTEWEG and N. H. SWELLENGREBEL.
(From the Institute of Tropical Hygiene, Amsterdam.)

(Communicated at the meeting of June 29, 1929.)

I. *Introduction.* By W. A. P. SCHÜFFNER.

1. *Korteweg's hypothesis.*

The manifestation of fever in malaria is generally held to be strictly controlled by the process of merogony of *Plasmodium* in the human host, as it is wholly dependent on the presence of a certain minimum number of parasites in the circulation. In *Pl. vivax* this minimum amounts to 20—50 parasites¹⁾ per cub. mm. It is reached 10—20 days after the infection, by each sporulating parasite, of 5—10 successive generations, yielding 10—20 merozoites every other day. Consequently, the length of the incubation of malaria is a function of the number of merozoites and of the period of the sporulation. As these two factors are fairly constant, the length of incubation can vary only within narrow limits.

As early as 1902 KORTEWEG's observations threw some doubt on the general applicability of this view. Among his patients some had never suffered from malaria and others a very long time ago. Among these groups of men he observed numerous cases of malaria in March—May, at the time of low anopheline density preceding the hatching of the first summergeneration. Considering his intimate knowledge of the whole population of his semi-rural practice, the careful record he kept of all his cases, and his invariable habit to check his diagnosis by bloodexamination, his statement that these spring-cases are primary ones (and no relapses, as was asserted by others) carry particular weight. His conclusion, *that these cases are due to infections acquired during the previous autumn*, merited more attention than it actually gained, except among the doctors of the Zaanregion (VAN DER HORST, 1903, and our late lamented malarialogist SCHOO, 1905, among them), to whom this view became so familiar as to need no further proof.

2. *Confirmatory investigations.*

Apart from certain observations made during the war, where the interpretation is rendered doubtful owing to the possible application of quinine prophylaxis (FÜLLEBORN, 1924).

The investigation of this subject was taken up again by SWELLENGREBEL (1921, '22A, '24), showing *malarial infection in anopheles to be practically*

¹⁾ The so-called "pyrogenic limit".

confined to autumn and winter (without a corresponding rise in the human malarial incidence) and to be *almost absent during the height of the malarial season*.

KORTEWEG (1921) supported his hypothesis by new evidence, showing that individuals, living in houses where malaria occurred in early autumn, run a greater risk of catching malaria before June 1st. than others, an observation confirmed by HONIG (1922).

The study of experimental malaria in man, showing that the injection of malarious blood, during autumn and winter, causes a fever after an incubation of usual length, seemed clearly to disprove KORTEWEG's hypothesis. But JAMES and SHUTE (1926) showed, that this artificial transmission cannot be compared with the natural insect-transmission. For the latter frequently fails in autumn or winter, a circumstance which constitutes a serious obstacle to the introduction of insect-transmission in the practice of malarial treatment of paretics: The mental alienist naturally wishes his patients to catch malaria at a moment he judges to be the most propitious. If insect-transmission fails, he insists on the injection of malarious blood as a substitute. Unfortunately this attitude renders it very difficult to ascertain the subsequent history of paretics, who failed to develop malaria within the usual timelimits, after being subjected to insect-transmission in autumn or winter.

Nevertheless JAMES (1927) succeeded in tracing the history of such patients: one was bitten by infected *Anopheles* in November, two in December, the fourth one in February. *All four developed a typical malaria, but not before 6—9 months had passed.*

3. *Object of the present investigation.*

We deemed it of the highest importance to have these results confirmed .
 1^o. Because our psychiatrist and our venereologist, Prof. BOUMAN and Prof. MENDES DA COSTA had expressed their wish to have a regular supply of infected mosquitoes, as a means of treating special cases;
 2^o. To confirm KORTEWEG's hypothesis, because its further development, consequent upon SWELLENGREBEL's researches, had led already to practical applications in malarial control and, 3^o. had proved, moreover, useful in explaining the phenomenon of "anophelism without malaria" in the Netherlands. (SWELLENGREBEL 1922B, SWELLENGREBEL, DE BUCK and SCHOUTE 1927—1928, VAN THIEL 1922).

II. *Autumnal transmission, of malaria with normal incubation, by numerous bites of infected mosquitoes.*

By P. C. KORTEWEG.

1. *Explanatory remarks.*

The first point mentioned at the end of the preceding paragraph was my principal consideration, as we could not hope the mental alienist to take an interest in malarial infection of paretics by way of insect-transmission, unless we succeeded in applying this method all the year round.

For my transmission experiments I made use of two lots of infected mosquitoes,

2. Tabulated record of my transmission experiments.

| Patient. History of malaria | Bitten by mosquitoes of lot No. | Number of times infected anopheles were given an opportu- nity to feed | Number of well- ascertained infecting bites | Dates on which they were inflicted | Date on which commenced the fever | Date on which parasites were first detected | Incubation : in days | | Remarks |
|---|---------------------------------------|---|--|--|---|---|-------------------------|--------------|--|
| | | | | | | | maxi- mum | mini- mum | |
| K. no history of malaria | 2 | 14 | 5 | Oct. 30—Nov. 5 1928 | Nov. 11 1928 | Nov. 12 1928 | 12 | 6 | Male gametocytes on Nov. 23, 1928 |
| W. History of malaria 7 years ago | 2 | 41 | 9 | Oct. 29—Nov. 6 1928 | Nov. 14 1928 | Nov. 9 1928 | 16 | 8 | Spontaneous deferve- scence on Nov. 19. A few parasites remain till Dec. 17, 1928. |
| B. no history of malaria | 2 | 24 | 13 | Oct. 30—Nov. 3 1928 | Nov. 21 1928 | Nov. 24 1928 | 22 | 18 | |
| C. History of malaria 7—10 years ago | 2 | 45 | 8 | Nov. 2—22 1928 | no fever till Febr. 11 1929 | Nov. 15 1928 | — | — | Parasites found again on Nov. 22 and Dec. 10, 1928. Patient lost sight of since Febr. 11, 1929. |
| M. no history of malaria | 3 | 38 | 12 | Dec. 21 1928 Jan. 4 1929 | Jan. 9 1929 | Jan. 9 1929 | 19 | 5 | |

described as N^o. 2 and N^o. 3 in the next paragraph. In the following tabulated record, the expression "number of times infected Anopheles were given an opportunity to feed" means (as an instance) that, out of a lot of 10 anopheles, 3 were applied to the patient's skin for half an hour on the first, 3 on the second and 8 on the third day. The "number of well-ascertained infection bites" is the number of bites I myself saw inflicted by Anopheles, afterwards proved to be infected. This number is only a fraction of the number of infecting bites actually inflicted.

3. Conclusion.

These records show, that I succeeded four out of five times to cause a malarial fever to appear within the usual time-limits, after the bite of infected mosquitoes in autumn and winter. Considering, however, the heavy infection of the Anopheles I used (see next paragraph) and the number of bites they inflicted, this experiment cannot be regarded as a contradiction of my hypothesis on the autumnal origin of primary cases of malaria in spring.

III. Autumnal transmission, of malaria with protracted incubation, by one or two bites of infected mosquitoes.¹⁾

By N. H. SWELLENGREBEL, A. DE BUCK, C. E. DE MOOR, and
J. M. H. SWELLENGREBEL—DE GRAAF.

1. To imitate natural conditions, the infecting dose should be a light one.

In Holland the average number of infected Anopheles present in every 4 houses where malaria occurred, during the whole time infected mosquitoes are most numerous (September—December), amounts to no more than three. (SWELLENGREBEL, 1924). Some of these do not even carry sporozoites at the time of examination. Granting that most of them would have done so in due course, it still follows that an average of less than one Anopheles is available for malarial transmission in houses, sheltering parasite carriers among the human inhabitants.

To give KORTEWEG's hypothesis a fair trial it is, consequently, necessary to effect autumnal transmission by one single bite of a sporozoite carrier. Even with this precaution, the heavy infection of our Anopheles (half of them carried more than 49 zygotes; under natural conditions no more than one infected Anopheles in nine does so) and the fact that two of our subjects were bitten twice, were likely to influence unfavourably the result of our experiment.

2. Data concerning the infected mosquitoes.

The transmissions were effected with three lots of *A. maculipennis* (short-winged strain), infected with *Plasmodium vivax* (see table I).

¹⁾ These investigations were carried out under the auspices and with the financial support of the International Health Division of the Rockefeller Foundation.

TABLE I. *Details regarding the origin of the infected mosquitoes used in our experiments.*

| No. of lot | Number of anopheles | | Infecting bloodmeals ingested by the anopheles | | | Kind of food ingested by the mosquitoes on subsequent dates |
|------------|--|-------------------------------------|--|---|------------------------------|---|
| | A. surviving at the moment of maturation of the sporozoites | B. carrying salivary sporozoites | A. number of meals | B. number of male gametes per 1000 leucocytes | C. Dates of the ingestion | |
| 1 | 12 | 9 | 3 | 8—20 | Oct. 11—13, 1928 | Guineapig's blood only. |
| 2 | 18 | 18 | 6 | the same gamete carrier as in N ^o . 1. | Oct. 11—13 and 15—17, 1928 | Human blood only. |
| 3 | 7 | 5 | 3 | 7—10 | Nov. 27—29, 1928 | Guineapig's blood only. |

Note: The human gamete-carrier infecting lot 1 and 2 had been infected, himself, by the injection of blood, containing plasmodia, which had been transmitted in this artificial way, without interruption, for passages. The carrier, infecting lot 3, was KORTEWEG's patient "K", himself infected by insect-transmission.

The feeding of recently infected mosquitoes on guineapig's blood did not check the development of the parasite, a confirmation of OTTOLENGHI and BROTZU's results (1928). The number of infected *Anopheles* in lot 1 was less than in lot 2; but this is accounted for by the number of infecting meals in the latter being twice that in the former. It will be remarked that the bite of the mosquitoes of lot 1 invariably caused malaria after a prolonged incubation, those of lot 2 usually after an incubation of normal length. This might be explained by a lessened vitality of the sporozoites, developed in mosquitoes fed on non-human blood. But this explanation cannot be upheld; for our subject N^o. 4 was also bitten by a mosquito of lot N^o. 2 (fed on human blood exclusively). Moreover KORTEWEG's patient "M" was successfully infected (maximal incubation 21 days) by mosquitoes of lot 3, fed on guinea-pigs like lot 1.

3. *Data relative to the individuals infected in autumn, 1928.*

Owing to the difficulties encountered in this kind of experiments, when carried out with paretics, we employed a number of healthy subjects, who volunteered to be bitten by mosquitoes of lot N^o. 1 (one also by a mosquito of lot N^o 2).

They were:

1^o. W. A. P. SCHÜFFNER; frequently acquired malaria while living in Sumatra. His last attack occurred in 1921. Lives in Holland since 1922. — 2^o. P. C. KORTEWEG; suffered from simple tertian between 1880 and 1885 (acquired in Holland) but never since that time. — 3^o. J. M. H. SWELLENGREBEL—DE GRAAF; had two attacks (subtertian and simple tertian) of malaria in Sumatra, 1917 and three (simple tertian) in Java, the last one in September 1918. Lives in Holland since 1920. — 4^o. N. H. SWELLENGREBEL; had two attacks (simple- and subtertian) in Sumatra, 1917, one (simple tertian) in Java, 1918, the last one (subtertian) in Java, January 1919. Lives in Holland since 1920, but frequently visits highly malarious localities (the last time in October 1928); never caught malaria on these tours (N.B.: no prophylactic quinine). — 5^o. A. DE BUCK; never had malaria, always lived in Holland. — 6^o. C. E. DE MOOR; like N^o. 5.

All these individuals inhabit localities in the province of North-Holland where malaria

is extremely rare; moreover, in the endemic regions of this province, malaria is very rare since 1923. Subject N^o. 1 may have acquired an infection December 1928 in Cairo: N^o. 4, October 1928 in Bulgaria. But if the malaria they developed this summer owes its origin to these hypothetical infections and not to the real ones they acquired experimentally, this fact needs not alter our conclusions.

We conclude, accordingly, that the attacks of malaria from which these individuals suffered in the summer of 1929, were caused by the bite of infected *Anopheles* in the autumn of 1928.

4. Record of transmissions.

Every *Anopheles*, biting one of our subjects, was dissected immediately afterwards to ascertain the extent of the infection of the salivary glands. The results of our experiments are collected in Table II.

TABLE II. *Tabulated record of our transmission experiments.*

| Serial number of subject | Number of bites inflicted by infected anopheles | Origin and degree of salivary infection of biting anopheles | Date of infecting bite | Fever occurring on: | Parasites detected on: | Incubation | Remarks (Parasites 7:1000 means 7 Parasites per 1000 leucocytes) |
|--------------------------|---|---|-------------------------------|-----------------------|------------------------|--|---|
| 1 | Once | Lot 1. Heavily infected | Oct. 30, 1928 | June 26, 28, 1929 | June 28, 1929 | 7 months 27 days | Tertian fever. Parasites 7:1000. |
| 2 | Once (without drawing blood). | Lot 1. moderately infected | Oct. 31, 1928 | July 6—9, 1929 | July 6—10, 1929 | 8 months 6 days | Quotidian remittent fever ¹⁾ Parasites 54—580:1000. |
| 3 | Twice | Lot 1. heavily infected | Nov. 1, 1928 | July 15, 17, 1929 | July 17, 18, 1929 | 8 months 15 days | Tertian fever. Parasites 132—204:1000. |
| 4 | Twice | <div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 2em; vertical-align: middle; margin-right: 5px;">{</div> <div> Lot 1. heavily infected Lot 2. heavily infected </div> </div> | Oct. 30, 1928 Dec. 5, 1928 | July 20—26, 1929 — | July 20—26, 1929 — | 8 months 18 days (7 months 16 days) | (Male gametes on July 23, 25, in small numbers; Parasites 2—124:1000. Quotidian intermittent fever. |
| 5 ²⁾ | Once | Lot 1. heavily infected | Nov. 7, 1928 | July 23—26, 1929 | July 23, 25, 26, 1929 | 8 months 15 days | Quotidian remittent fever changing into tertian intermittent. Parasites 1—2:1000. |
| 6 | Once | Lot 1. moderately infected | Nov. 2, 1928 | Aug. 2—4, 1929 | Aug. 3, 5, 1929 | 8 months 30 days | Quotidian remittent fever. On Aug. 4th complete intermission. Parasites very few to 39:1000. |

¹⁾ KORTEWEG's (1924) "initial malarial fever".

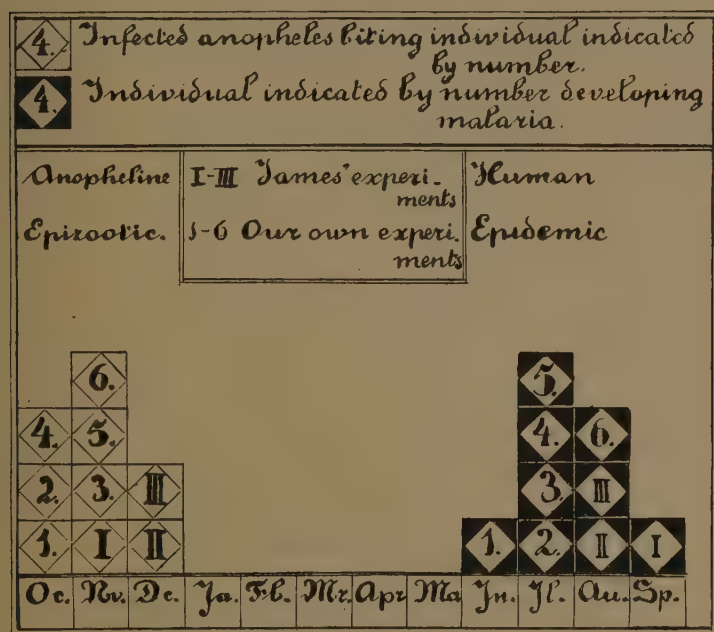
²⁾ This case is remarkable for the number of parasites remaining well below the pyrogenic limit for the greater part of the fever period, although the successive paroxysms ran up to 38°.4, 40°.0 and 40°.3.

5. Precautions against overlooking slight attacks.

During the three weeks following the infecting bites, temperatures were taken thrice a day and thick films examined at frequent intervals. Later on, all our subjects closely watched their state of health; temperatures were taken and bloodfilms examined on the slightest provocation. In no case parasites were detected previous to the attacks mentioned in Table I. Only N^o. 1 showed a pigmented leucocyte (but no parasites) on May 13, 1929. Consequently, the attacks of fever from which our subjects suffered cannot be taken as relapses of slight undetected attacks, occurring shortly after the infecting bite or later on¹).

6. Summary.

The accompanying diagram, showing the combined result of JAMES' (except for the case infected in February²)) and our own experiments,



may serve as a graphical summary of both. It is a model on a small scale of a summer-epidemic of human malaria, arising from an autumnal epizootic

¹) This does not imply, that primary cases with prolonged incubation can be identified with those showing an incubation of normal length. The appearance of male gametocytes in N^o. 4 suggests that these two are not the same.

²) Although there are still infected mosquitoes, human infections in Holland are unlikely to occur in February. Experiments to infect mosquitoes in that month were much less successful than in autumn (4 infected ones on 36 Anopheles, no sporozoite-carriers), owing to the high mortality consequent upon a precocious development of the eggs.

of anopheline malaria. The model is not a perfect one, as the maximum of the "epidemic" should have fallen in May or June instead of July. This suggests, that the majority of autumnal infections are acquired in September and October, not in November and December¹).

On the other hand our experiments demonstrate, that autumnal anopheline infection not only accounts for malaria occurring before, but also after the first of June²). This evidence suggests, that the more important part of the annual malarial epidemic, i.e. the portion occurring before the second half of July, is due to infections acquired during the preceding autumn.

REFERENCES.

- FÜLLEBORN (1924). Verhändl. d. Tropenmediz. Abt. d. Deutsch. Kolonialkongr. Arch. f. Sch. u. Trop. Hyg. Leipzig, 28, pp. 505—509.
- HONIG (1922). Studie over de malaria te Nieuwendam en omgeving. Amsterdam, J. H. DE BUSSY, 78 pp.
- HORST, VAN DER (1903). Latente infectie of recidief? Ned. Tijdschr. v. Geneesk., Amsterdam, 34, 1st half, N^o. 6, pp. 306—309.
- JAMES and SHUTE (1926). Report on the first results of laboratory work on malaria in England. League of Nations, Health Organisation, Geneva, C. H. Malaria (57), 30 pp.
- JAMES (1927). Communication made to the Health Committee, League of Nations, Geneva, Session of October 26, 1927.
- KORTEWEG (1902). Klinische observaties over malaria in den winter van 1901—'02. Herinneringsbundel voor Prof. ROSENSTEIN. Leiden, E. IJDO, pp. 263—281.
- (1921). Wanneer heeft ten onzent malariabesmetting plaats? (1st communication). Nederl. Tijdschr. v. Geneesk., Haarlem, 65, 2nd half, N^o. 12, pp. 1485—'86.
- (1924). De aanvangskoorst der malaria tertiana. Ibid., 68, 1st half, N^o. 15, pp. 1622—1638.
- OTTOLENGHI and BROTZU (1928). Intorno all' eventuale azione di pasti eterologhi sulla sviluppo del parassita nell' anofele. Riv. di Malariologia, Roma, 7, N^o. 6, pp. 849—852.
- SCHOO (1905). Malaria in Noord-Holland. Haarlem, F. BOHN, 361 pp.
- SWELLENGREBEL (1921). Wanneer heeft ten onzent malariabesmetting plaats? (2nd communication). Nederl. Tijdschr. v. Geneesk., Haarlem, 65, 2nd half, N^o. 12, pp. 1486—88.
- (1922 A). Fréquence saisonnière des Anophèles impaludés aux environs d'Amsterdam. Bull. Soc. Pathol. Exot., Paris, 15, N^o. 2, pp. 116—119.
- (1922 B). Het overwinteren van A. maculipennis in de omgeving van Amsterdam. Tijdschr. v. Vergel. Geneesk., Leiden, 7, N^o. 4, pp. 297—303.
- (1924). Nadere bijzonderheden over de herfst- en winterbesmettingen met malariaparasieten van A. maculipennis om Amsterdam. Nederl. Tijdschr. v. Geneesk., Haarlem, 68, 2nd half, N^o. 6, pp. 750—763.

¹) This is in striking accordance with KORTEWEG's hypothesis, but somewhat at variance with the monthly prevalence of infected Anopheles, which is higher, on an average, in November and December, viz. 5%, than in September and October, viz. 4% (SWELLENGREBEL 1924).

²) This date (marking the hatching of the first summer generation of Anopheles) was formerly considered as a critical one, the beginning of the renewed activity of Anopheles as malarial vectors, consequent upon their increased numbers. At present we know (SWELLENGREBEL, DE BUCK and SCHOUTE 1929), that the Anopheline density, which reaches a minimum in May, does not markedly increase till the end of July (hatching of the second summer generation).

SWELLENGREBEL, DE BUCK and SCHOUTE (1927). On anophelism without malaria around Amsterdam; 1st communication. *Proc. Roy. Acad. of Science, Amsterdam*, **30**, N^o. 1, pp. 61—68.

————— (1928). On anophelism without malaria around Amsterdam; 2nd communication. *Ibid.*, **31**, N^o. 4/5, pp. 531—539.

————— (1929). On anophelism without malaria around Amsterdam; 3rd communication: On the food of adult *Anopheles* in malarious and non-malarious regions. *Ibid.*, **32**, N^o. 6, pp. 772—779.

THIEL, VAN (1922). *Anopheles* en malaria in Leiden en naaste omgeving. *Acad. Proefschr.* Leiden, S. C. v. DOESBURGH.

Physics. — *The properties of the Ni-Cu alloys at low temperatures.*

By A. KRUPKOWSKI and W. J. DE HAAS. (Communication N^o. 194a from the Physical Laboratory, Leiden).

(Communicated at the meeting of September 29, 1928).

The properties of the *Ni-Cu* alloys at room temperature and at higher temperatures were described by W. GUERTLER and G. TAMMANN ¹⁾, N. S. KURNAKOW and S. F. ZEMCZUZYNY ²⁾.

The melting-curve of these alloys was investigated by H. GAUTIER ³⁾; the electric properties were determined by K. FEUSSNER ⁴⁾ and E. SEDSTRÖM ⁵⁾; the thermal dilatation was measured by C. H. JOHANSSON ⁶⁾; röntgenographic researches were made by A. SACKLOWSKI ⁷⁾.

During the last years P. CHEVENARD ⁸⁾ has investigated these alloys at temperatures between -200° and 1000° ; mostly with self-registering apparatus. From his experiments we know, that the transition from the ferro- to the paramagnetic series of alloys shows some irregularities, which are distinctly observable at very low temperatures.

The purpose of this investigation was the study of the behaviour of the *Cu-Ni*-alloys down to the hydrogen-temperature region.

The alloys used for these researches were prepared in the metallurgic laboratory of the technical highschool Warsaw either in the form of rods of 17 cm. length and 5 mm. diameter or as drawn wires.

The materials used for the preparation of these alloys were electrolytic copper and nickel, prepared by the MOND procedure. For the investigation of the properties of the pure metals electrolytic nickel and electrolytic copper were used and also electrolytic copper melted in a hydrogen atmosphere.

For the measurements with alloys in cast state these were melted in a hydrogen atmosphere and annealed during 6 days in vacuum at a temperature of $+900^{\circ}$. The alloys for these wires were melted in the ordinary atmosphere under a protecting layer of BaCl_2 with a little admixture of charcoal; after having been rolled and drawn, they were

1) Z.S. f. Anorg. Chemie **52**, p. 25, 1907.

2) Z.S. f. Anorg. Chemie **54**, p. 150, 1907.

3) C.R. **123**, p. 172, 1896.

4) Verh. d. Phys. Ges. **10**, p. 109, 1891.

5) Ann. d. Phys. **59**, p. 134, 1919.

6) Ann. d. Phys. **76**, p. 445, 1925.

7) Ann. d. Phys. **77**, p. 241, 1925.

8) Journ. of the Inst. of Met. **26**, p. 39, 1926.

annealed during 3 days in vacuum at a temperature of 750–850°. The homogeneity of the alloys was determined under the microscope.

Electric resistance measurements.

The resistance of the wires and of some rods was measured with the DIESELHORST compensation box. In order to be able to determine the specific resistance accurately the diameter of each wire was measured at 20 places between the copper wires (soldered to it for the potential measurements). Then the wires were put in the cryostat. The measurements were made at 0°, –183°, –205°, –252°,5 and –258°,4. The temperature was determined very accurately with the Pt -resistance thermometer.

Table A contains the results of the measurements. In this table not only the resistances ϱ_t are given but also the ratio $\frac{\varrho_t}{\varrho_0}$ and the mean resistance coefficient $L = \frac{\Delta\varrho_t}{\varrho_0 \cdot \Delta t}$, where $\Delta\varrho_t$ is the change in the resistance, corresponding with the temperature interval Δt . Finally ϱ_0 is the resistance at 0°.

Fig. 1 represents the conductivity-curve. The form of the curve is

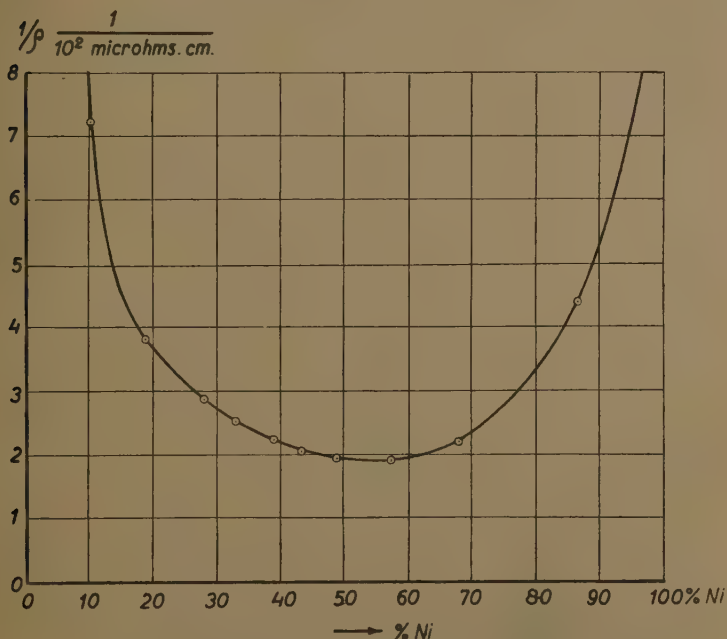


Fig. 1. Weight % Ni. The specific conductivity of the Ni—Cu alloys in the form of wires.

characteristic for pure mixed crystals and shows no appreciable curvature at the transition from ferro- to paramagnetic alloys.

Fig. 2 gives the resistance of the different alloys at a function of the temperature. In some of the curves a point of curvature occurs, which the measurements of P. CHEVENARD and also our thermo-magnetic measurements showed to correspond exactly with the Curie-point of the alloys, that is with the point, where these change from paramagnetic into ferro-magnetic.

For the alloys with 43.45%, 48.40%, 57.45% nickel the Curie-points lie resp. at about -247° , -196° , -97° (the last value was derived from thermo-magnetic measurements).

The change of the resistance at low temperatures is very small. Only for those alloys which have their Curie-points at very low temperatures i.e. for the alloys with 43.45% Ni and with 48.40% Ni is this change considerable. This is evident from the curves of the mean resistance coefficient represented in figs. 3—14. The thick horizontal lines represent the mean resistance coefficients, while the curves give the interpolated true resistance coefficients as a function of the temperature.

The curves resistance coefficient-percentage nickel show at oxygen-temperature a maximum towards the side of high copper-content. This maximum decreases with increasing percentage of nickel, remaining however observable down to 38% Ni.

We cannot yet say with certainty, whether this increase of the resistance coefficient is connected with a general change in the properties of the metal alloys or that it occurs as an anomaly in the case of Cu-Ni alloys only.

Fig. 2. The specific resistances of the Ni—Cu alloys in the form of wires.

between -192° and $+500^{\circ}$. From his tables we conclude that only for copper has an increase of the resistance coefficient been found at the temperatures of liquid oxygen.

¹⁾ Ann. d. Phys. 73, p. 145, 1919.

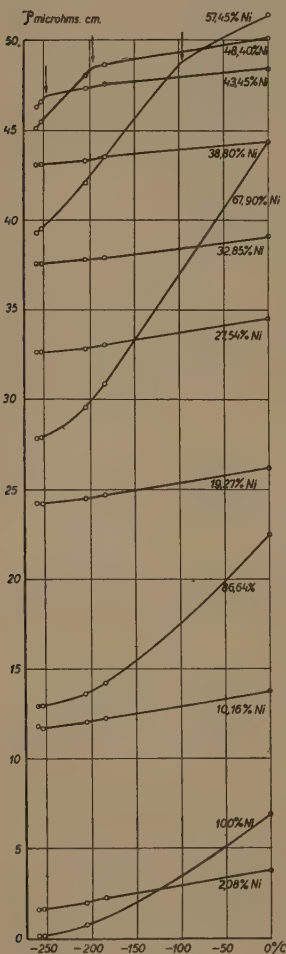


TABLE A.

| $N^1)$ | Weight % $\frac{2}{2}$ Cu | Weight % $\frac{2}{2}$ Ni | Length/mm. | Diameter/ mm. | Temperature t | Specific. res. micro- ohm cm. ρ_t | Resistivity ratio $\frac{\rho_t}{\rho_0}$ | Mean coeff. of resistivity of L 10^4 | Mean temperature |
|--------|------------------------------|------------------------------|------------|------------------|--------------------|--|---|--|---------------------|
| 2.d | 97.92 | 2.08 | 130.2 | 0.935 | 0 | 3.8676 | 1 | 21.897 | — 91.55 |
| | | | | | —183.10 | 2.3177 | 0.59926 | 28.688 | —193.96 |
| | | | | | —204.82 | 2.0767 | 0.53695 | 20.975 | —228.71 |
| | | | | | —252.60 | 1.6891 | 0.43673 | 2.708 | —255.37 |
| | | | | | —258.14 | 1.6833 | 0.43523 | | |
| 4.d | 89.84 | 10.16 | 135.4 | 1.057 | 0 | 13.8039 | 1 | 5.956 | — 91.18 |
| | | | | | —182.35 | 12.3049 | 0.89140 | 6.299 | —193.46 |
| | | | | | —204.56 | 12.1118 | 0.87741 | 3.541 | —228.55 |
| | | | | | —252.54 | 11.8752 | 0.86042 | —0.553 | —255.44 |
| | | | | | —258.33 | 11.8816 | 0.86074 | | |
| 6.d | 80.73 | 19.27 | 126.7 | 0.949 | 0 | 26.2314 | 1 | 3.107 | — 91.41 |
| | | | | | —182.81 | 24.7414 | 0.94319 | 3.462 | —194.09 |
| | | | | | —205.37 | 24.5365 | 0.93538 | 1.336 | —228.95 |
| | | | | | —252.52 | 24.3712 | 0.92908 | —2.162 | —255.48 |
| | | | | | —258.44 | 24.4048 | 0.93036 | | |
| 7.d—1 | 72.46 | 27.54 | 119.4 | 0.984 | 0 | 34.5377 | 1 | 2.310 | — 91.18 |
| | | | | | —182.35 | 33.0830 | 0.95788 | 2.796 | —193.46 |
| | | | | | —204.56 | 32.8685 | 0.95167 | 1.165 | —228.55 |
| | | | | | —252.54 | 32.6754 | 0.94608 | —1.088 | —255.44 |
| | | | | | —258.34 | 32.6970 | 0.94671 | | |
| 8.d—1 | 67.15 | 32.85 | 129.8 | 0.990 | 0 | 39.2349 | 1 | 1.652 | — 91.55 |
| | | | | | —183.10 | 38.0489 | 0.96977 | 2.058 | —193.96 |
| | | | | | —204.82 | 37.8733 | 0.96530 | 1.184 | —228.76 |
| | | | | | —252.63 | 37.6515 | 0.95964 | —0.723 | —255.40 |
| | | | | | —258.16 | 37.6669 | 0.96004 | | |

1) N — d wires. N rods.

2) Composition from copper analysis.

TABLE A (Continued).

| N | Weight o/o Cu | Weight o/o Ni | Length/ mm. | Diameter/ mm. | Temperature t | Specific res. micro- ohm cm. ρ_t | Resistivity ratio $\frac{\rho_t}{\rho_0}$ | Mean coeff. of resistivity of L 10^4 | Mean temperature |
|--------|------------------|------------------|----------------|------------------|--------------------|---|---|--|---------------------|
| 10.d | 61.20 | 38.80 | 131.3 | 0.992 | 0 | 44.4510 | 1 | 1.070 | — 91.51 |
| | | | | | -183.01 | 43.5804 | 0.98041 | 1.863 | —194.10 |
| | | | | | -205.18 | 43.3967 | 0.97628 | 1.069 | —228.86 |
| | | | | | -252.53 | 43.1719 | 0.97122 | 1.416 | —255.46 |
| | | | | | -258.39 | 43.1348 | 0.97039 | | |
| 11.d | 56.55 | 43.45 | 118.6 | 1.021 | 0 | 48.4480 | 1 | 0.914 | — 91.50 |
| | | | | | -183.00 | 47.6376 | 0.98327 | 2.275 | —194.10 |
| | | | | | -205.19 | 47.3932 | 0.97822 | 3.078 | —228.86 |
| | | | | | -252.53 | 46.6870 | 0.96365 | 10.837 | —255.46 |
| | | | | | -258.38 | 46.3799 | 0.95731 | | |
| 12.d | 51.60 | 48.40 | 128.7 | 1.053 | 0 | 50.1182 | 1 | 1.553 | — 91.40 |
| | | | | | -182.80 | 48.6904 | 0.97151 | 5.255 | —194.09 |
| | | | | | -205.37 | 48.1011 | 0.95975 | 10.926 | —228.97 |
| | | | | | -252.52 | 45.5189 | 0.90823 | 11.233 | —255.48 |
| | | | | | -258.44 | 45.1860 | 0.90158 | | |
| 13.d—1 | 42.55 | 57.45 | 126.5 | 0.985 | 0 | 51.4360 | 1 | 8.312 | — 91.55 |
| | | | | | -183.10 | 43.6117 | 0.84788 | 13.365 | —193.96 |
| | | | | | -204.82 | 42.1184 | 0.81885 | 10.580 | —228.71 |
| | | | | | -252.60 | 39.5185 | 0.76830 | 6.462 | —255.37 |
| | | | | | -258.13 | 39.3342 | 0.76472 | | |
| 15.d—1 | 32.10 | 67.90 | 128.7 | 0.992 | 0 | 44.4493 | 1 | 16.616 | — 91.52 |
| | | | | | -183.04 | 30.9304 | 0.69586 | 12.342 | —194.06 |
| | | | | | -205.07 | 29.7221 | 0.66867 | 7.966 | —228.80 |
| | | | | | -252.52 | 28.0419 | 0.63087 | 3.242 | —255.45 |
| | | | | | -258.38 | 27.9572 | 0.62897 | | |

TABLE A (Continued).

| N | Weight % Cu | Weight % Ni | Length/mm. | Diameter/ mm. | Temperature t_f | Specific. res. micro- ohm cm. ρ_t | Resistivity ratio $\frac{\rho_t}{\rho_0}$ | Mean coeff. of resistivity $L \cdot 10^4$ | Mean temperature |
|--------|------------------|------------------|------------|------------------|----------------------|--|---|---|---------------------|
| 19.d-1 | 13.36 | 86.64 | 126.4 | 0.984 | 0 | 22.5152 | 1 | 20.045 | — 91.42 |
| | | | | | -182.83 | 14.2637 | 0.63351 | 11.755 | —194.10 |
| | | | | | 205.37 | 13.6663 | 0.60698 | 6.280 | —228.95 |
| | | | | | -252.52 | 12.9996 | 0.57737 | 1.402 | —255.49 |
| | | | | | -258.43 | 12.9810 | 0.57654 | | |
| 23.d | 0 | 100 | — | — | 0 | 6.9330 ¹⁾ | 1 | 45.188 | — 91.22 |
| | | | | | -182.44 | 1.2174 | 0.17559 | 28.618 | —192.75 |
| | | | | | -203.06 | 0.8083 | 0.11658 | 16.007 | —227.82 |
| | | | | | -252.57 | 0.2588 | 0.03733 | 4.281 | —255.46 |
| | | | | | -258.34 | 0.2417 | 0.03486 | | |
| 14 | 40 ²⁾ | 60 ²⁾ | — | — | 0 | | 1 | 11.409 | — 91.18 |
| | | | | | -182.35 | 0.79196 | | 13.414 | —193.45 |
| | | | | | -204.55 | 0.76218 | | 9.440 | —228.55 |
| | | | | | -252.54 | 0.71688 | | 4.870 | —255.44 |
| | | | | | -258.33 | 0.71406 | | | |
| 15 | 35 | 65 | — | — | 0 | | 1 | 16.477 | — 91.22 |
| | | | | | -182.44 | 0.6994 | | 12.221 | —192.75 |
| | | | | | -203.06 | 0.6742 | | | |
| 18 | 20 | 80 | — | — | 0 | | 1 | 20.516 | — 91.18 |
| | | | | | -182.36 | 0.62587 | | 11.964 | —193.46 |
| | | | | | -204.55 | 0.59932 | | 6.620 | —288.55 |
| | | | | | -252.54 | 0.56755 | | 1.433 | —255.44 |
| | | | | | -258.33 | 0.56672 | | | |
| 21 | 5 | 95 | — | — | 0 | | 1 | 30.059 | — 91.22 |
| | | | | | -182.44 | 0.4516 | | 18.808 | —192.76 |
| | | | | | -203.07 | 0.4128 | | | |

1) This value has been taken from FLEMING. Proc. Royal Soc. 66, p. 51, 1899.

2) Composition according to the synthesis.

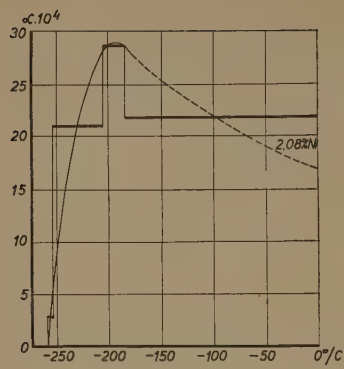


Fig. 3.

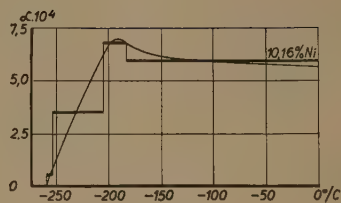


Fig. 4.

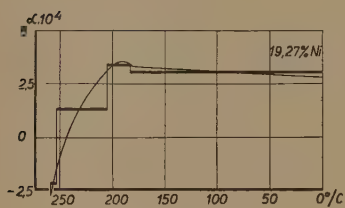


Fig. 5.

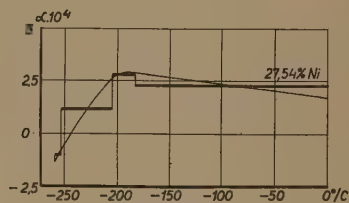


Fig. 6.

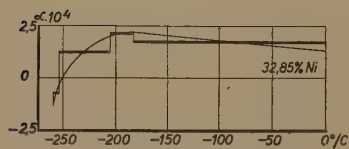


Fig. 7.

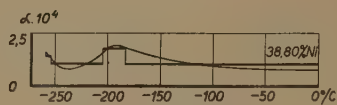


Fig. 8.

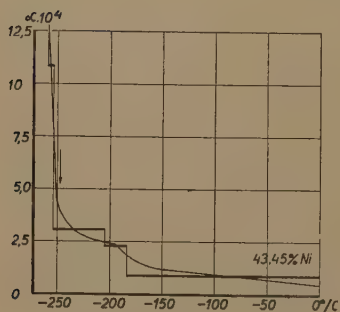


Fig. 9.

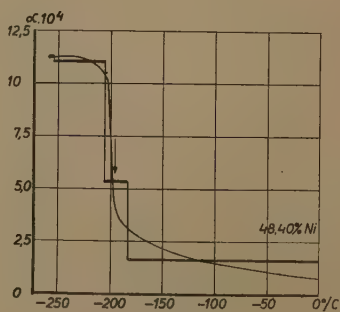


Fig. 10.

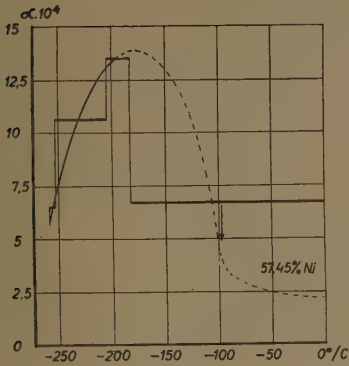


Fig. 11.

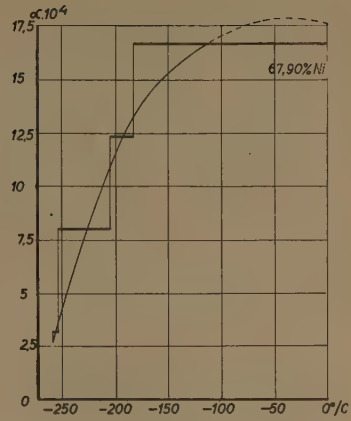


Fig. 12.

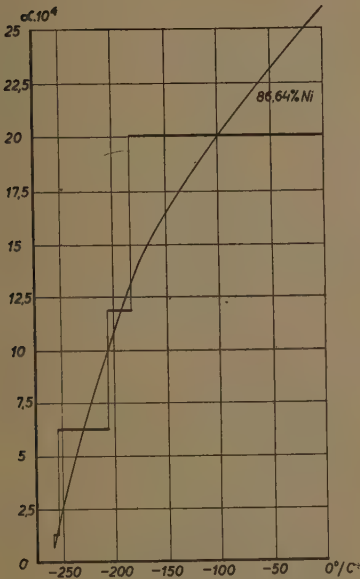


Fig. 13.

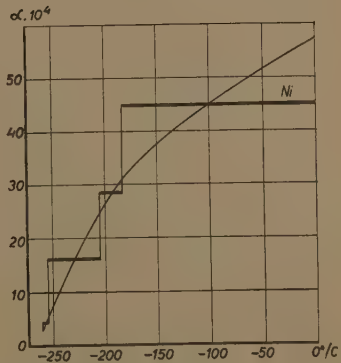


Fig. 14.

Fig. 3—14. The mean and true resistance coeff. of the Ni—Cu alloys as a function of the temperature.

We find a strong increase of the resistance coefficient for those alloys which pass from the ferro- into the paramagnetic state viz. for those with 43.45%, 48.40% and 57.45% Ni. It is very interesting that the resistance coefficient always increases in the ferromagnetic region and

does not have its maximum at the Curie-point but at much lower temperatures.

For the alloys with a nickel percentage from about 12 % till 35 % we find negative resistance coefficients between -258.4° and -252.5° .

Fig. 15 represents the mean resistance coefficients as a function of the composition of the alloys.

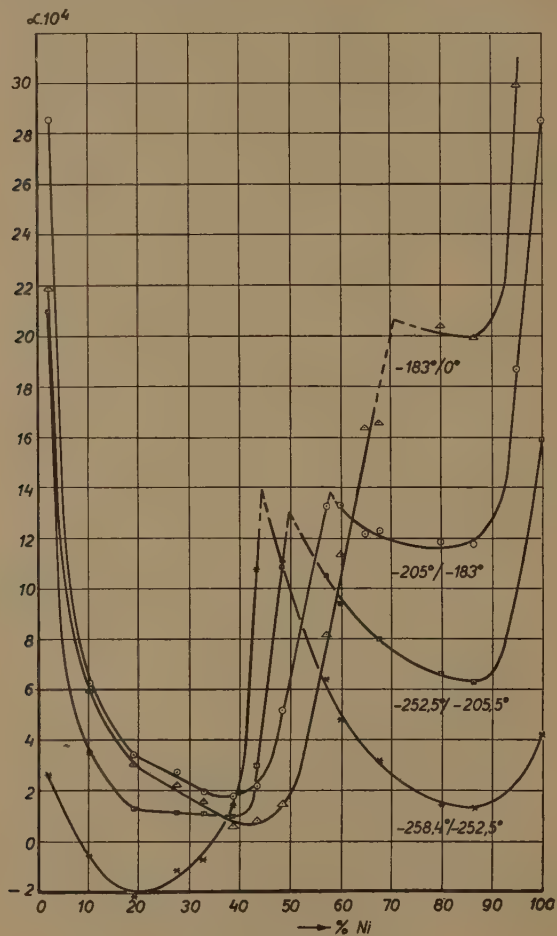


Fig. 15 (weight % Ni).

It is evident, that a decrease of temperature displaces the maximum in the direction of a low nickel content and that the absolute value of the mean resistance coefficients is nearly constant and approximately equal to $14 \cdot 10^{-4}$.

Physics. — *Thermo-electric and dilatation determinations with Ni-Cu alloys at low temperatures.* By A. KRUPKOWSKI and W. J. DE HAAS. (Communication N^o. 194*b* from the Physical Laboratory, Leiden).

(Communicated at the meeting of October 27, 1928).

§ 1. *Thermo-electric measurements.*

One extremity of the wire of the Cu-Ni alloy was placed in ice at 0° C. and the other in the cryostat. Both extremities were soldered to a copper wire and thus formed a thermo-element.

From the thermo-forces alloy-copper measured in this way the thermo-forces alloy-lead were derived with the aid of the known thermo-forces copper-lead. Our results are given in table B. We see, that the thermo-

TABLE B.

| N | Weight % Cu | Weight % Ni | Temperature region | Thermo-force in microvolt alloy or lead- copper | Thermo-force in microvolt alloy or lead- copper per degree | Thermo-force in microvolt alloy-lead per degree | Mean temperature |
|------|----------------|----------------|--------------------|--|--|--|---------------------|
| Lead | — | — | 0/—182.72 | + 406.3 | — 2.224 | — | — 91.36 |
| | | | —182.72/—203.34 | + 42.8 | — 2.076 | — | —193.03 |
| | | | —203.34/—252.57 | + 90.3 | — 1.834 | — | —227.96 |
| 2.d | 97.92 | 2.08 | 0/—183.10 | +1079.0 | — 5.896 | — 3.672 | — 91.55 |
| | | | —183.10/—204.82 | + 70.1 | — 3.227 | — 1.151 | —193.96 |
| | | | —204.82/—252.60 | + 103.7 | — 2.170 | — 0.336 | —228.71 |
| 4.d | 89.84 | 10.16 | 0/—182.36 | +2403.8 | —13.182 | —10.958 | — 91.18 |
| | | | —182.36/—204.53 | + 147.8 | — 6.667 | — 4.591 | —193.45 |
| | | | —204.53/—252.55 | + 244.5 | — 5.091 | — 3.257 | —228.54 |
| 6.d | 80.73 | 19.27 | 0/—182.72 | +3504.8 | —19.181 | —16.957 | — 91.36 |
| | | | —182.72/—203.34 | + 224.6 | —10.892 | — 8.816 | —193.36 |
| | | | —203.34/—252.57 | + 336.5 | — 6.835 | — 5.001 | —227.96 |

TABLE B (Continued).

| N | Weight o/o Cu | Weight o/o Ni | Temperature region | Thermoforce in microvolt alloy or lead- copper | Thermoforce in microvolt alloy or lead- copper per degree | Thermoforce in microvolt alloy-lead per degree | Mean temperature |
|--------|------------------|------------------|--------------------|---|---|---|---------------------|
| 7.d-1 | 72.46 | 27.54 | 0/—182.36 | +4183.8 | —22.942 | —20.718 | — 91.18 |
| | | | —182.36/—204.53 | + 278.4 | —12.557 | —10.481 | —193.45 |
| | | | —204.53/—252.55 | + 385.8 | — 8.034 | — 6.200 | —228.54 |
| 8.d-1 | 67.15 | 32.85 | 0/—183.10 | +4797.4 | —26.213 | —23.989 | — 91.55 |
| | | | —183.10/—204.82 | + 295.2 | —13.591 | —11.515 | —193.96 |
| | | | —204.82/—252.60 | + 469.7 | — 9.830 | — 7.996 | —228.71 |
| 11.d | 56.55 | 43.45 | 0/—182.72 | +5075.4 | —27.777 | —25.553 | — 91.36 |
| | | | —182.72/—203.34 | + 331.1 | —16.057 | —13.981 | —193.03 |
| | | | —203.34/—252.57 | + 513.0 | —10.420 | — 8.586 | —227.96 |
| 12.d | 51.60 | 48.40 | 0/—182.72 | +5083.2 | —27.820 | —25.596 | — 91.36 |
| | | | —182.72/—203.34 | + 339.4 | —16.460 | —14.384 | —193.03 |
| | | | —203.34/—252.57 | + 522.4 | —10.611 | — 8.777 | —227.96 |
| 13.d-1 | 42.55 | 57.45 | 0/—183.10 | +4732.5 | —25.859 | —23.635 | — 91.55 |
| | | | —183.10/—204.82 | + 364.2 | —16.768 | —14.692 | —193.96 |
| | | | —204.82/—252.60 | + 542.1 | —11.346 | — 9.512 | —228.71 |
| 15.d-1 | 32.10 | 67.90 | 0/—182.72 | +4814.0 | —26.346 | —24.122 | — 91.36 |
| | | | —182.72/—203.34 | + 342.3 | —16.600 | —14.524 | —193.03 |
| | | | —203.34/—252.57 | + 514.2 | —10.445 | — 8.611 | —227.96 |
| 19.d-1 | 13.36 | 86.64 | 0/—182.72 | +3972.3 | —21.740 | —19.516 | — 91.36 |
| | | | —182.72/—203.34 | + 219.2 | —10.630 | — 8.554 | —193.03 |
| | | | —203.34/—252.57 | + 306.8 | — 6.232 | — 4.398 | —227.96 |

force per degree strongly decreases at low temperatures and seems to approach to zero at the absolute zero-point.

Fig. 1 represents the curve of the mean thermo-forces per degree for alloy-lead. In two of the curves a small maximum is perceptible, nearly

exactly corresponding with the Curie-point. A decrease of the temperature diminishes the absolute value of this maximum.

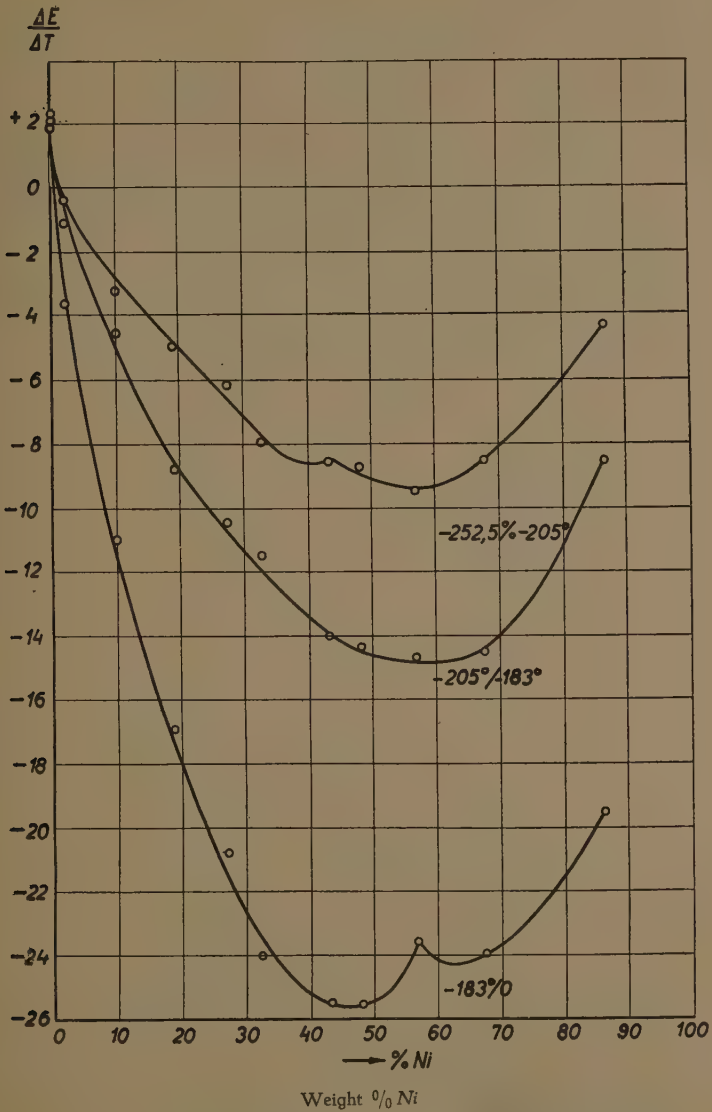


Fig. 1. The mean thermoforce of the Ni-Cu alloys-lead per degree

The ordinates $\frac{\Delta E}{\Delta T}$ in microvolts per degree.

§ 2. Thermal dilatation.

The thermal dilatation was measured with the apparatus of W. BRONIEWSKI (fig. 2). Part of this apparatus is a quartz tube (Q_2) containing the rod (e), 10 cm. long, that is to be investigated. The quartz rod (Q_1) touches this rod at one side, and fits at the other side into a small conical hole of the lever (B). This lever carries two small steel needles (N), one of which rests in a small excavation in the upper plate of the apparatus, while the other rests in a groove. Further the mirror L is attached to the lever.

At a distance of ca. 2 m. a glass scale and a small electric lamp with incandescent filament are mounted. The light emitted by the lamp falls on the mirror and reflects the image of the filament on the scale. When heated the rod e is dilated and raises the lever B . The displacement of the image on the scale is a measure of the dilatation. The screw S serves to fix the quartz tube. The pen-shaped pieces of copper F keep the rod e motionless.

When the rod is placed in Q_2 and the whole apparatus is ready, the

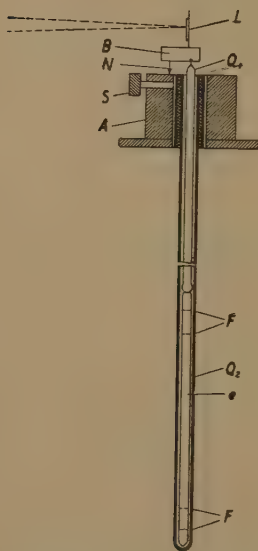


Fig. 2. The dilatation apparatus.

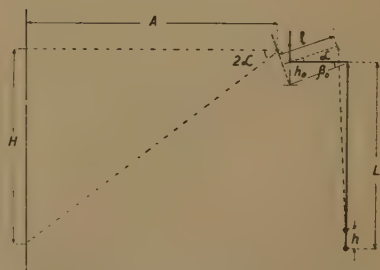


Fig. 3. The scheme of the dilatation apparatus.

lower part is cooled down to the derived temperatures in different vacuum glasses. The deflection of the image on the scale is always noted.

The apparatus was calibrated by means of a ZEISS micrometer. By several measurements it was established that a deflection of the image on the scale from $H_1 = 99.9$ mm. to $H_2 = 484.3$ mm. exactly corresponds

to 0,500 mm. The distance from the scale to the lever was $A = 2042$ mm., the length of the needles $h_0 = 4.64$ mm.

These values, put in the formulae

$$H = A \operatorname{tg} 2L$$

$$h = e \sin (L + \beta_0)$$

give

$$e = 7410,64^9$$

$$\beta_0 = 38^\circ, 45, 88^1.$$

The absolute value of the dilatation with respect to quartz

$$h_2 - h_1 = l \left\{ \sin \left(\frac{1}{2} \operatorname{arc} \operatorname{tg} \frac{H_1}{A} + \beta_0 \right) - \sin \left(\frac{1}{2} \operatorname{arc} \operatorname{tg} \frac{H_2}{A} + \beta_0 \right) \right\}$$

can be calculated from two readings on the scale H_2 and H_1 ; corresponding with the temperatures t_2 and t_1 . The mean dilatation coefficient with respect to quartz between the temperatures t_2 and t_1 is

$$a = \frac{h_2 - h_1}{l(t_2 - t_1)}.$$

During the measurements with liquid oxygen Q_2 was placed in a Dewar glass with alcohol; after one hour the temperature of this bath was noted. Then this alcohol bath was replaced by a vacuumglass with liquid oxygen and after about half an hour, when Q_2 had reached the temperature of this bath, the deflections on the scale and the barometric height were read.

During the measurements with liquid hydrogen the whole apparatus was first placed in an evacuated Dewar glass. After one hour the beginning temperature and the position of the image on the scale were read. Then liquid hydrogen was poured into the vessel and the displacement of the image on the scale noted.

The temperature was calculated from the pressure, under which the hydrogen was boiling in the cryostat. In this way the mean dilatation coefficients with respect to quartz between room temperature and the temperature of boiling oxygen and also between room temperature and the temperature of boiling hydrogen can be determined.

The obtained values for the mean coefficients were reduced to the mean room temperature of 10° .

From the dilatation coefficients thus obtained for electrolytic copper with respect to quartz, combined with the absolute values of this dilatation coefficient according to KEESOM, VAN AGT and Miss JANSEN¹⁾, we found the mean dilatation coefficient of the quartz used between 10° and -183° and between 10° and $-252,6^\circ$.

¹⁾ Comm. Lab. Leiden N^o. 182.

These values were subtracted from the values obtained for the mean dilatation coefficients of the alloys with respect to quartz. The mean values thus found for the absolute dilatation coefficients of different alloys in cast form are to be found in table C.

TABLE C.

| N | Weight % Cu | Weight % Ni | Mean linear dilatation coefficient with respect to quartz between 10° and -252.6° $\times 10^6$ | Mean true linear dilatation coefficient between 10° and -252.6° $\times 10^6$ | Mean linear dilatation coefficient with respect to quartz between 10° and -183° $\times 10^6$ | Mean true linear dilatation coefficient between 10° and -183° $\times 10^6$ | Mean true linear dilatation coefficient between -183° and -252.6° $\times 10^6$ |
|------|-------------|-------------|---|---|---|---|---|
| 1 | 100 | 0 | 11.96 | 11.68 | 14.34 | 14.08 | 5.04 |
| 2 | 98 | 2 | 11.80 | 11.52 | 14.21 | 13.95 | 4.78 |
| 4 | 90 | 10 | 11.56 | 11.28 | 13.68 | 13.42 | 5.21 |
| 5 | 85 | 15 | 11.30 | 11.02 | 13.34 | 13.08 | 4.69 |
| 6 | 80 | 20 | 10.98 | 10.70 | 13.11 | 12.85 | 4.73 |
| 7 | 75 | 25 | 10.62 | 10.34 | 12.82 | 12.56 | 4.19 |
| 8 | 70 | 30 | 10.46 | 10.18 | 12.75 | 12.49 | 3.79 |
| 9 | 65 | 35 | 10.27 | 9.99 | 12.64 | 12.38 | 3.35 |
| 10 | 60 | 40 | 10.12 | 9.84 | 12.40 | 12.14 | 3.47 |
| 11 | 55 | 45 | 9.96 | 9.68 | 12.35 | 12.09 | 3.00 |
| 12 | 50 | 50 | 10.01 | 9.73 | 11.98 | 11.72 | 4.16 |
| 12-1 | 47.5 | 52.5 | 9.78 | 9.50 | 11.89 | 11.63 | 3.60 |
| 14 | 40 | 60 | 9.55 | 9.30 | 11.57 | 11.31 | 3.74 |
| 15 | 35 | 65 | 9.39 | 9.11 | 11.73 | 11.47 | 2.55 |
| 17 | 25 | 75 | 9.05 | 8.77 | 11.23 | 10.97 | 2.65 |
| 18 | 20 | 80 | 8.85 | 8.57 | 11.03 | 10.77 | 2.46 |
| 19 | 15 | 85 | 8.71 | 8.43 | 11.99 | 10.73 | 2.05 |
| 21 | 5 | 95 | 8.49 | 8.21 | 10.56 | 10.30 | 2.40 |
| 23 | 0 | 100 | 8.38 | 8.10 | 10.38 | 10.12 | 2.51 |

Fig. 4 represents the curve of the mean dilatation coefficient between 10° and -183° as a function of the nickel percentage. We see a slight bending at about 65 % Ni. On the curve of the mean dilatation coeffi-

cient between 10° and -252.6° the bending point is displaced towards the copper side, actually to ca. 50 % Ni.

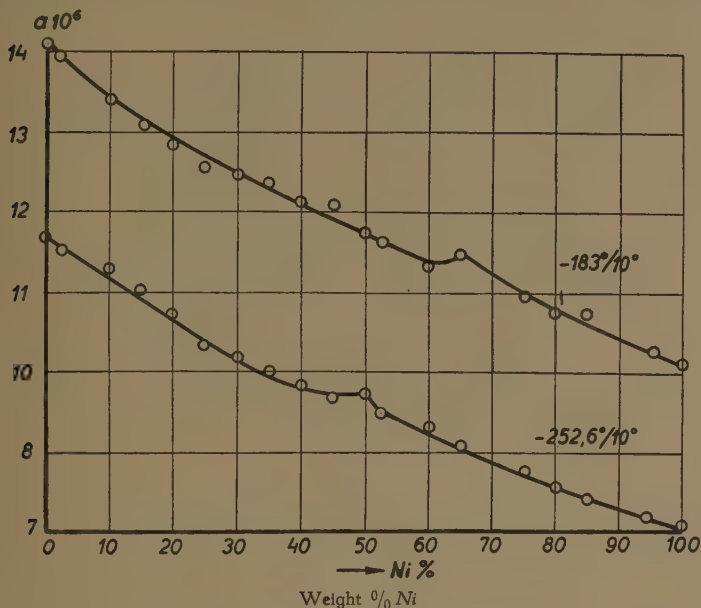


Fig. 4. The mean linear dilatation coefficient of the Ni-Cu alloys between 10° and -183° and between 10° and -252.6° .

Fig. 5 gives the mean dilatation coefficient of the alloys between -183° and -252.6° derived from the curves of the other two mean values.

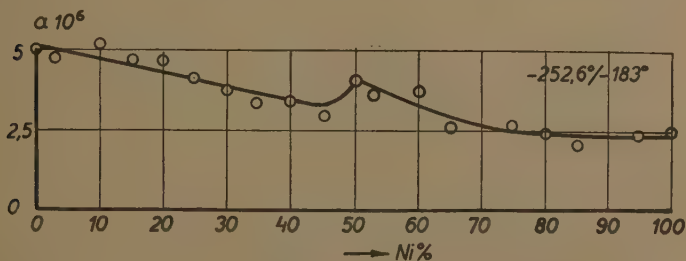


Fig. 5. The mean linear dilatation coefficient of the Ni-Cu alloys between -183° and -252.6° .

The above mentioned slight bending is connected with the transition from the para- into the ferro-magnetic state. Its meaning is, that at this transition the alloys are thermally differently dilatant in the ferro-magnetic than in the paramagnetic state. The consequence is in agreement

with the results of P. CHEVENARD for pure nickel. The results of C. H. JOHANSSON also give a slight bending point, which however nearly always lies within limits of the possible errors.

§ 3. Conclusions.

Fig. 6 gives the final results.

Curve I represents the boundary between para- and ferro-magnetic alloys.

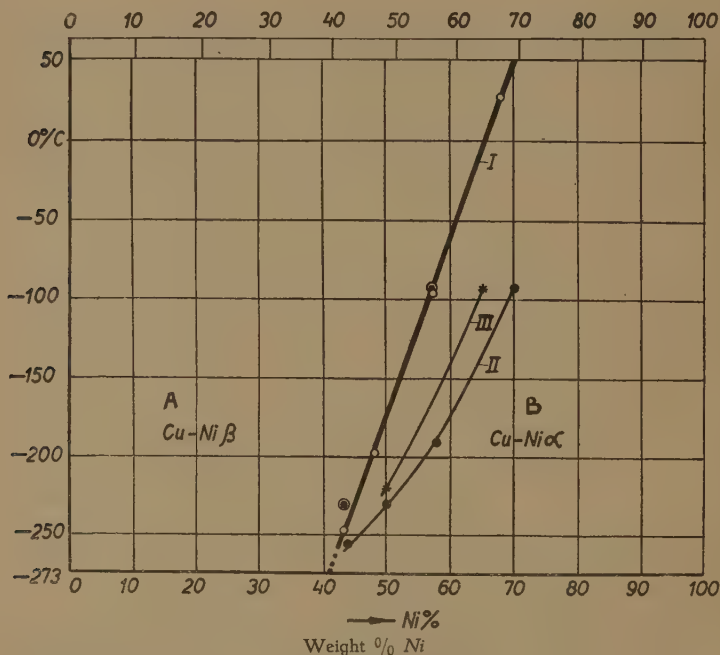


Fig. 6. Diagram of the curve of magnetic transition I, of the curve of the maximum mean resistance coefficients II and of the curve of the maximum mean thermal dilatation coefficients III.

○ bending points of the electric resistances.

• maximum points of the thermo-forces.

A region of mixed crystals Cu-Ni β.

B " " " " Cu-Ni α.

From this figure it is evident, that the bending points of the resistance curves (o) and also the points of the maximum thermo-forces • coincide on the curve of magnetic transition. This curve is a straight line, the prolongation of which gives for the absolute zero-point a composition of about 41 weight % Ni or 43 atom % Ni.

Curve II is drawn through the points of maximum value of the mean

resistance coefficient. This curve is displaced with respect to curve I. This means that the maximum of the change of resistance does not exactly agree with the Curie-point, but is displaced towards the region of low temperatures.

Curve II is not a straight line. At low temperatures it approaches the line of the magnetic transitions.

Curve III joins the points that represent the maximum values of the mean dilatation coefficients. It lies between the two preceding curves.

From the above mentioned investigations it is evident, that in the interval from 100% to 43 at % Ni every alloy undergoes a magnetic change, which in a more or less complicated way gives rise to a change in its physical properties, so that the bending points on the curves that represent these properties either correspond with the Curie-points (e.g. resistance, thermo-force) or are more or less displaced (e.g. mean resistance coefficient and mean dilatation coefficients).

This fact is not only no proof for the existence of a chemical compound, but even one against it.

Summary.

I. In the electric investigations with Cu-Ni alloys here described the curve of the magnetic transition points was determined down to hydrogen temperature. The prolongation of this straight line cuts the composition axis at ca. 43 atm. % Ni.

II. The bending points on the curves of the mean resistance coefficient and of the mean dilatation coefficient lie on the low temperature-side with respect to the first line.

Geology. — *The rocks of the Katmai Region (Alaska).* By W. F. GISOLF.

(Communicated at the meeting of September 28, 1929)

In a previous article ¹⁾ I explained that the lavas of the Etna volcano at Sicily can be considered as heteromorphic rocks of diorites with a composition of plagioclase and amphibole. Use was made of a graphical method based on the Nigglian tetrahedron and parameters, modified by BECKE ²⁾ and the present writer ³⁾. The great advantage of this method, over every other method, is that it enables directly to estimate the possible mineral compositions of a rock or of a series of rocks, superior analyses being at hand.

The rocks of the Katmai region occur as lava-flows, sills, dikes, necks, plugs and ancient intrusive masses. There are several volcanos in the district, Mt. Katmai, Mt. Mageik, Mt. Martin, Knife Peak Volcano,

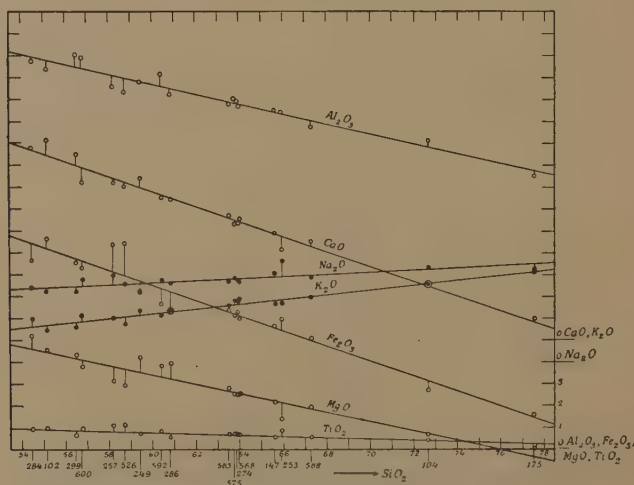


Fig. 1. Straight line variation diagram of the Katmai rocks (after Fenner).
The numbers of the analyzed specimens, given at the bottom of the figure,
correspond with those of Fenner.

¹⁾ W. F. GISOLF. Die Laven vom Etna. These Proceedings **31**, p. 660, 1927.

²⁾ F. BECKE. Graphische Darstellungen von Gesteinsanalysen. T. M. P. M. **37**. p. 27. 1925.

³⁾ W. F. GISOLF. Zur graphischen Darstellung von Gesteinsanalysen. T. M. P. M. **39**. p. 76. 1928.

requires in all cases smoothing of the lines ; the smaller the smoothing the more content the petrologist. But by smoothing lines the care of much laboratory work becomes useless and one realises, that Nature is being wronged.

Applying the method which has been used in my paper on the Etna-lavas, I came to the results laid down in Table I. The graph is shown in

TABLE I. Nigglian parameters of the Katmai-rocks.

| Nº. | Nº. coll. Fenner. | Si | 2 fe ₂ O ₃ | feo | mgo | c | al | na | ka |
|-----|----------------------|-----|----------------------------------|------|------|------|------|------|------|
| 1 | 284 | 145 | 6.1 | 11.5 | 20.8 | 23.7 | 27.9 | 8.4 | 1.6 |
| 2 | 102 | 149 | 7.6 | 11.4 | 18.4 | 25.9 | 27.7 | 8.2 | 0.8 |
| 3 | 297 | 157 | 6.5 | 11.6 | 18.1 | 24.7 | 29.6 | 8.5 | 1.0 |
| 4 | 600 | 168 | 14.0 | 4.3 | 16.7 | 21.1 | 31.3 | 10.4 | 2.2 |
| 5 | 257 | 176 | 4.7 | 16.4 | 14.1 | 21.9 | 29.6 | 11.3 | 2.0 |
| 6 | 526 | 186 | 10.4 | 12.5 | 13.7 | 21.2 | 30.4 | 10.4 | 1.4 |
| 7 | 249 | 179 | 4.7 | 11.9 | 18.8 | 23.4 | 29.7 | 9.0 | 2.5 |
| 8 | 592 | 194 | 2.4 | 13.6 | 18.3 | 19.8 | 32.3 | 11.2 | 2.4 |
| 9 | 286 | 198 | 7.7 | 8.1 | 19.3 | 18.9 | 32.2 | 11.0 | 2.8 |
| 10 | 583 | 224 | 5.9 | 11.3 | 14.7 | 20.0 | 32.8 | 11.9 | 3.4 |
| 11 | 575 | 230 | 6.0 | 10.6 | 13.6 | 19.0 | 33.9 | 12.8 | 4.1 |
| 12 | 274 | 230 | 6.1 | 11.3 | 13.5 | 19.3 | 33.8 | 12.1 | 3.9 |
| 13 | 568 | 230 | 10.4 | 6.0 | 13.8 | 19.8 | 33.2 | 12.5 | 4.3 |
| 14 | 147 ¹⁾ | | | | | | | | |
| 15 | 253 | 265 | 3.9 | 14.3 | 8.3 | 15.3 | 36.4 | 17.5 | 4.3 |
| 16 | 588 | 272 | 6.4 | 9.5 | 11.7 | 17.8 | 35.1 | 14.4 | 5.1 |
| 17 | 104 | 371 | 3.1 | 7.5 | 5.0 | 13.1 | 42.2 | 20.6 | 8.5 |
| 18 | 175 | 498 | 2.3 | 5.5 | 0.0 | 7.0 | 47.3 | 25.0 | 12.9 |

Fig. 3. Before calculating the Nigglian parameters from the molecular quotients, the accessory minerals, with the exception of magnetic and ilmenite, were eliminated. Apatite is a phosphate and not a silicate ; in silicate diagrams it should be eliminated ; if this is not done, it contaminates the results. Titanium can be neglected or added to silica ; the ore being represented in that case as FeO or FeSiO₃ and not as FeTiO₃, which does not matter.

From the graph may be seen that :

1. The poles in the al-alk-field lie in an almost straight line.

¹⁾ This analysis is omitted: P₂O₅ and Al₂O₃ not being separated.

2. The poles in the silica-field lie in a nearly straight line, but not so nearly as the poles in the al-alk-field.

3. The poles in the c-fm-field have the same character of distribution as the silica-poles.

The character of these lines indicates that all the rocks of the Katmai region can be considered as heteromorphic rocks of diorites composed of plagioclase, amphibole and free quartz. As there is no analysis of any amphibole of this region, I am free to choose the composition of the amphibole. I have come to good results with an amphibole with the composition $A_1T_5M_{14}nSiO_2$ ($A = Na_2O + K_2O$, $T = Al_2O_3$, $M = CaO + MgO + FeO + 2Fe_2O_3$); although better results can probably be obtained with an amphibole somewhat richer in alkalies and alumina; but that is of no importance for the general considerations hereafter. The composition of the amphibole and the plagioclase for every rock can be calculated from the diagram in a simple manner. The results have been laid down in Table II; the values have been calculated from and controlled in the graph. The behavior of the free silica is very peculiar; its quantity decreases or increases proportionally to the quantity of alkalisfelspar. This is not only the case for the Katmai region; in future papers I will describe similar cases from other localities.

This behavior of the silica suggests that the composition of the alkali felspar may, in this case, be written as $(Na, K)_2O Al_2O_3 12 SiO_2$ and not, as usual $(Na, K)_2O Al_2O_3 6 SiO_2$. It suggests the possibility of stability of such compound with high pressure¹⁾ (with perhaps negative combining heat). An exception to this behavior of the silica is afforded by N^o. 18. Probably the excess of silica in N^o. 18 is due to desilification of deeper magma, of which N^o. 15 is an example. Both rocks have been erupted by the Katmai Volcano.

When using the values of Table II, it should be remembered: 1st that the plagioclases are written as $m CaO Al_2O_3 2 SiO_2 + n(Na, K)_2O Al_2O_3 12 SiO_2$ and 2nd that the ratio plagioclase: amphibole as read from the graph in Fig. 3, has relation to mineral molecules with the same amount of basic oxides; e.g. rock N^o. 257 (N^o. 5 in Table II) has the composition:

$18.4 \left[\frac{1}{10} \times (11 CaO Al_2O_3 2 SiO_2 + 89 (Na, K)_2O Al_2O_3 12 SiO_2) \right] + 81.6 \times [AlT_5 M_{14} 16 SiO_2]$. The number of basic oxides in the plagioclase is:

$\frac{1}{10} (2 \times 11 + 2 \times 89) = 20$; in the amphibole it is $1 + 5 + 14 = 20$ too.

¹⁾ The great many intergrowths of alkalisfelspar and quartz may be remembered (myrmekite and micropegmatite). Myrmekite goes as far as andesine. The circumstances under which these intergrowths occur, suggest high pressure. It is suggested that decrease of pressure originates the allknown structures.

TABLE II.

| N ^o . | N ^o . coll. Fenner. | Parameters of the amphiboles: $\frac{al_1=25}{alk_1=5}$ | | | | $\frac{o}{100}$ Anorthite in plagioclase ¹⁾ | Ratio Plagioclase: Amphibole | Locality |
|------------------|-----------------------------------|---|---|----------------|-------------------|--|------------------------------------|-------------------------|
| | | mgo ₁ | (2fe ₂ o ₃ +feo) ₁ | c ₁ | si ₁ | | | |
| 1 | 284 | 23.5 | 19.9 | 26.6 | 89 | 4 | 11.6:88.4 | Old volcanic neck. |
| 2 | 102 | 20.6 | 21.3 | 28.1 | 104 | 16 | 10.8:89.2 | Katmai Crater. |
| 3 | 299 | 25.0 | 25.0 | 20.0 | 102 | 41 | 18.4:81.6 | Ancient sill. |
| 4 | 600 | 22.3 | 24.5 | 23.2 | 64 | 30 | 25.2:74.8 | Knife Peak. |
| 5 | 257 | 17.2 | 25.9 | 26.9 | 80 | 11 | 18.4:81.6 | Katmai Crater. |
| 6 | 526 | 17.0 | 29.2 | 23.8 | 109 | 25 | 21.6:78.4 | " " |
| 7 | 249 | 23.2 | 20.4 | 26.4 | 106 | 21 | 18.8:81.2 | " " |
| 8 | 592 | 25.8 | 22.6 | 21.6 | 91 | 31 | 29.2:70.8 | Ancient intrusive mass. |
| 9 | 286 | 27.1 | 20.8 | 22.1 | 94 | 29 | 28.8:71.2 | Ancient intrusive mass. |
| 10 | 583 | 21.4 | 25.0 | 23.6 | 108 | 24 | 31.2:69.8 | Mt. Mageik. |
| 11 | 575 | 21.1 | 25.8 | 23.1 | 89 | 23 | 31.6:69.4 | " " |
| 12 | 274 | 21.0 | 26.7 | 22.3 | 104 | 27 | 35.2:64.8 | Mt. Martin |
| 13 | 568 | 20.5 | 24.4 | 25.1 | 93 | 18 | 32.8:67.2 | Mt. Mageik. |
| 14 | 147 | — | — | — | — | — | — | Isolated hill. |
| 15 | 253 | 15.3 | 33.5 | 21.2 | 53 ²⁾ | 16 | 45.6:54.4 | Katmai Crater. |
| 16 | 588 | 20.0 | 26.7 | 22.3 | 111 | 18 | 40.4:59.6 | Ancient intrusive mass. |
| 17 | 104 | 16.0 | 34.0 | 20.0 | 86 | 20 | 68.8:31.2 | Katmai Crater. |
| 18 | 175 | 0.0 | 62.5 | 7.5 | 337 ²⁾ | 16 | 89.2:10.8 | Katmai Crater. |

It is not necessary, that all the amphiboles are stable compounds (e.g. N^o. 15 and 18 Table II); evidence is brought for the existence of the complexon $A_1T_5M_{14}$ (or near to that) in the underlying magma. This complex needs for its complete saturation 24 SiO₂ or si₁ = 120. The results of Table II are plotted in Fig. 4 and Fig. 5. From these graphs may be seen, that the rocks of Katmai, Mageik and the ancient rocks behave differently.

¹⁾ The plagioclase is written as $mCaO \cdot Al_2O_3 \cdot 2SiO_2 + n(Na,K)_2O \cdot Al_2O_3 \cdot 12SiO_2$ ($m+n=100$).

²⁾ The deficit of silica in the amphibole of N^o. 15 may be the cause of the excess in silica in N^o. 18.

The magma or the magmas of the Katmai Volcano itself has or have differentiated much more than the magmas of the other eruption points; and it may be for that reason, that the rocks of the Katmai Volcano give the best poles for an ordinary variation diagram ¹).

As all the rocks of the Katmai region can be considered as heteromorphous

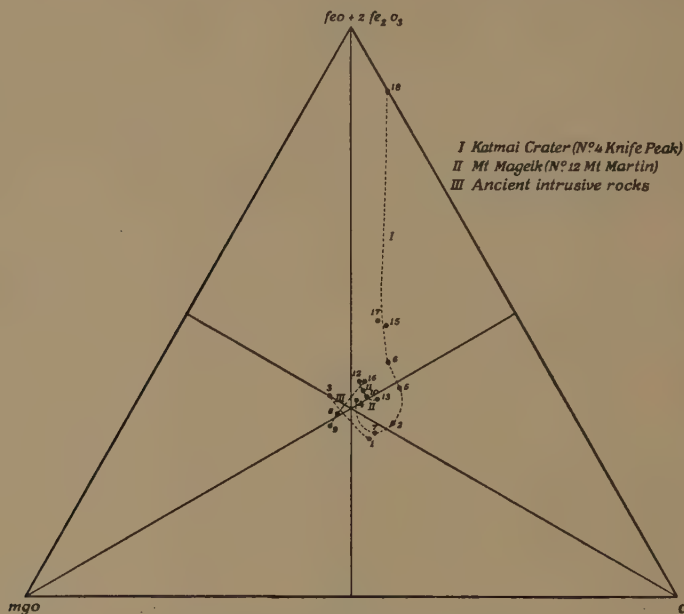


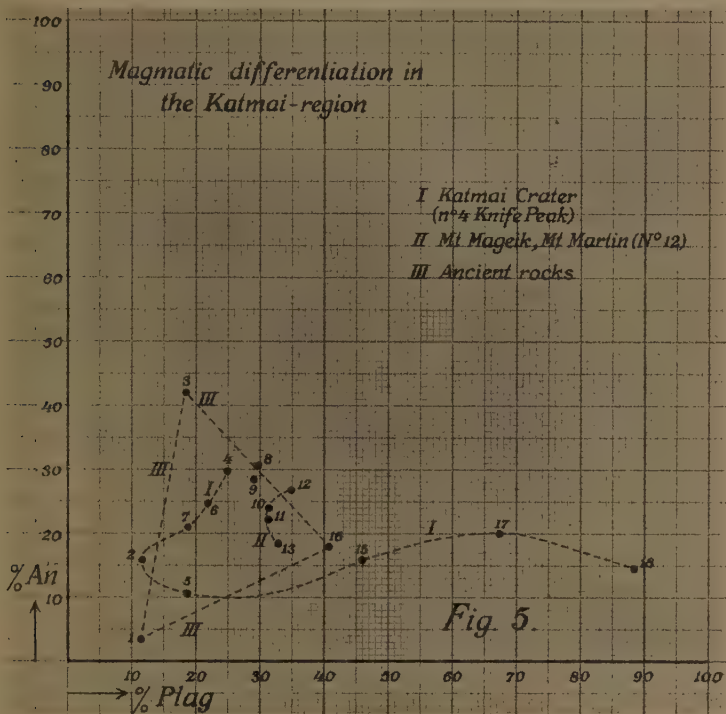
Fig. 4.
Composition of the amphiboles, with regard to
 $MgO, FeO + 2 Fe_2O_3, CaO$.

rocks of diorites, composed of plagioclase and amphibole, it follows that the whole original magma must have had a same composition. But after the views of modern petrology, such a magma would differentiate in a total different manner, and it does now, as may be derived from the occurrence of olivine-basalts.

I can only see two ways out of this difficulty: 1st to reject the evidence, given to us by Nature and 2nd to assume that all the lavas and intrusive rocks had different magmas, which once were all part of a huge mass of solid (quartz) dioritic rock, itself part of a differentiated huger magma. This quartz-dioritic rock must have been molten up in parts by some process (release of pressure, heating from beneath, radioactivity); each part having its own lavastreams. In this connection it is very interesting

¹) In my next paper, on the rocks of Tahiti, I will give a general reason for the fact that volcanic effusive rocks show magmatic differentiation better than intrusive rocks.

to see in Fig. 4, that the amphibole in the heteromorphic quartz-diorites of the rocks 9, 8, 3, 1 have the largest amount in magnesia and that these rocks are the oldest igneous rocks of the region. It may be suggested, that



in the huge quartz-dioritic mass these rocks were the deepest (to explain their content of magnesia) and that heating from beneath together with release of pressure ¹⁾ may have attacked these rocks first, made them liquid and sent them into the fissures of the earth crust, healing these fissures at the moment they were created. The same considerations hold for the lavas of the Etna volcano.

In close connection with the problem of differentiation stands the sinking of crystals advocated by BOWEN, as it seems when reading his publications superficially; but all that he requires for his theory of differentiation is that crystals, once into being, do not react further with the liquid. They must be taken away. But sinking of crystals suggests a steady rain of crystals in downward direction; and just at the moment, when a certain

¹⁾ By passing the Davison layer of no stress downward, which will be done first by the deepest rocks; or, which leads to the same effect, by the moving upward of the Davison-layer.

part of the liquid has lost its crystals, other crystals are coming from above; lavas without crystals will be abnormal; unless crystals are solved in the liquid; but then the liquid is contaminated, not pure, mother liquor; glassy rocks will lose their value for the theory of BOWEN.

To solve this difficulty, it is necessary to remember that the phase rule can only be applied on systems which are homogeneous with regard both to temperature and to pressure; the system in a huge magmachamber can be homogeneous with regard to temperature, but never with regard to pressure. At the bottom of every layer of about 3 m. thickness, the pressure is one atmosphere more than at the top. As has been demonstrated by famous physicists this increase of pressure has but a very slight influence upon concentration; but it can and must have a large influence upon the place, where crystallisation starts.

Crystallisation of silicates probably involves diminution of volume; increase of pressure diminishes the solubility of silicates; the first crystals will be born at or close to the bottom of the magmachamber. There will be no rain of crystals; the liquid is taken away from the crystals; the liquid, having lost its heavier components and perhaps acquired some crystallisation heat, will rise and mix up with the other liquid. Aphanitic lavas will generally represent true mother liquor and will be normal. A part of the liquid, having lost some crystals at the bottom, will vary much in composition, but being mixed up with the other liquid, the effect on the equilibrium of the crystals with the liquid will be very slight; whereas, crystals being formed in many places throughout the liquid, this will change its composition more rapidly and attack the rain of crystals.

This newer view does not alter much in BOWEN's theory and it explains more. If peridotites e.g. should be formed by sinking of crystals, a certain structure and idiomorphism should be the consequence. In the very pure peridotites of the Dutch East Indies (which are renowned for their huge peridotitic areas) every slide of peridotitic rock gives the impression that the rock has crystallised in place; there is no idiomorphism at all.

The origin of granophyric structures within gabbros, too, can be explained. As everybody knows, from ordinary crystallising solutions, hollows can be formed in the crystal mass, filled up with mother liquor. This may not only be the case in the laboratory but also in Nature. Such an imprisoned part of the mother liquor will be much influenced by the increase of pressure in its own body¹⁾ than the huge mass of mother liquor outside. It will differentiate in its own manner by cooling only; the last liquid will be rich in potash and silica; granophyric structures in gabbros can be looked for as often as liquid inclusions in masses of rock salt. The greatest difference between the genesis of the two kinds of granophyre viz, that occurring in gabbros and that occurring in granites is, that the concentration of the gases in the gabbro-granophyre is very small and in the granite-granophyre probably very large. The

¹⁾ Because of its much smaller dimensions.

consequence is shown in the occurrence of pyroxene in the gabbro granophyre and of hornblende and biotite in the granite-granophyre. This explanation is a very strong support to the theory which attributes the origin of granitic rocks to the differentiation of basaltic magma.

If cooling of the crystallised mass does not go too rapid, release of pressure (e.g. the cracking of the massif by cooling) may be the cause of liquefaction of the deeper rocks, especially when these rocks contain solid compounds unstable with lower pressure (e.g. solid solutions of substances with low molecular weight, ordinarily designed as gases, or other compounds). This may be the explanation of the origin of many basaltic dikes in the granites of the Archean regions in Northern Europe and elsewhere; where basaltic dikes came into being before the granites had solidified entirely. It may be part of the solution, too, for the problem of volcanic action in the Etna-, Katmai- and in many other regions.

Of course the newer views, explained in this paper, have an important bearing on geophysical problems ; the intimate connection between volcanic and tectonic actions, the floating of continents, isostasy, the peridotitic shell, the reconciliation between the two most important theories on the figure of the Earth, the theory of the secular cooling of the Earth of James Hall and the TAYLOR-WEGENER theory, and so on. But that will be the subject of a future paper.

Bandoeng, 19 Juli 1929.

Medicine. — *Etudes sur la catatonie expérimentale. I. L'épreuve de la bulbocapnine chez la grenouille et la souris.* Par H. DE JONG (d'Amsterdam) et H. BARUK (de Paris). (Communicated by Prof. B. BROUWER.) (Travail du laboratoire de physiologie de la clinique neurologique de l'Université d'Amsterdam).

(Communicated at the meeting of September 28, 1929).

Dans un travail précédent¹⁾ nous avons montré que l'injection de bulbocapnine provoque chez le chat un syndrome moteur superposable au syndrome catatonique de l'homme.

Dans une récente communication M. DIVRY (de Liège)²⁾ émet certaines réserves sur nos conclusions en s'appuyant sur des expériences qu'il a faites non sur des chats, mais sur la grenouille et la souris. Il nous a donc semblé intéressant de comparer l'effet de l'injection de la bulbocapnine chez ces deux derniers animaux avec celui que nous avons constaté chez le chat³⁾.

I.

Nous avons d'abord consacré une semaine à l'étude de l'action de la bulbocapnine chez la grenouille, en utilisant, afin de les comparer, une gamme de doses différentes. Au cours de ces expériences nous avons pu nous rendre compte combien il était difficile d'interpréter les réactions de la grenouille. Cet animal montré en effet à l'état normal un comportement très spécial que nous avons dû étudier avant de faire les injections.

Tout d'abord la grenouille présente une tendance spontanée à conserver une immobilité qui, en l'absence de stimulants, peut être absolue et prolongée. (Voir la fig. 1.)

Nous avons enregistré cette immobilité de la façon suivante : nous avons placé la grenouille sur un plateau de carton reposant sur une capsule à ressort, reliée par un caoutchouc à un Kymographe à rotation hélicoïdale et très lente, ce qui permet d'inscrire des tracés continus pendant un temps prolongé. Les mouvements de la grenouille sont indiqués sur les tracés par des dénivellations. La fig. 2 objective l'immobilité de la grenouille qui se traduit sur le tracé par une ligne rectiligne. Cette immobilité n'est d'ailleurs

¹⁾ DE JONG et BARUK. Etude comparative expérimentale et clinique des manifestations du syndrome catatonique. *Revue Neurologique*. Janvier 1929.

²⁾ P. DIVRY. A propos de la catalepsie bulbocapnique. *Journal de Neurologie et de Psychiatrie* N^o. 4. Avril 1929.

³⁾ Nous avons toujours pratiqué comme chez le chat des injections d'hydrochlorate de bulbocapnine en solution aqueuse, d' 1/100 HCl. normal dans des ampoules tyndalisées, préparées par M. KEULEMANS, pharmacien du Binnen-Gasthuis à Amsterdam.

interrompue ni par les bruits, ni par un défilé de couleurs (rouge vif par ex.) devant les yeux de l'animal, ni même par certaines menaces, comme d'approcher vivement le poing de l'oeil de la grenouille. Par contre les excitations tactiles provoquent de véritables réactions impulsives (sauts, bonds) qui peuvent devenir de plus en plus intenses et fréquentes si les excitations sont rapprochées. Le type moteur normal de ces amimaux est donc surtout caractérisé par un état d'akinésie spontanée entrecoupé de réactions impulsives et répétées à la suite des excitations.

Nous avons procédé sur six grenouilles à des injections de bulbo-capnine à des doses différentes. Voici le résumé des protocoles de nos expériences ;

Exp. 1.

15 juillet 1925. *Rana temporaria*, poids 64.11 gr.

17 h. 7 : Injection de 2.5 mgr. d'hydrochl. de bulbo-capnine dans le sac lymphatique du dos. Nous avons suivi cet animal toute la soirée en le comparant à une grenouille normale. Au début, il nous avait semblé que la grenouille paraissait un peu aplatie, le nez couché sur le sol, comme PETERS¹⁾ le décrit à la suite de l'injection de bulbo-capnine. Mais nous avons pu remarquer la même attitude dans tous ses détails chez la grenouille normale de comparaison. L'animal injecté fait d'ailleurs toujours des bonds normaux à la suite d'excitations.

Conclusion : Pas d'effet.

Exp. 2.

15 juillet 1929 gren. B.

17 h. 47. Injection de 3 mgr. de Hydr. chl. de bulbo-capn.

Résultats à peu près comme dans l'exp. 1. *Pas d'effet.*

Nous avons ensuite procédé à des injections de doses plus élevées.

Exp. 3.

16 juillet 1929. Gren. de 64.11 gr.

10 h. injection de 5 mgr. d'hydrochl. de bulbo-capn.

10 h. 07 excitation ; la grenouille saute, fait des bonds, dans l'eau. Une grenouille témoin est beaucoup plus immobile.

10 h. 30 même état.

15 h. Plus calme, pattes repliées. On peut écarter doucement les pattes qui ne se replient ensuite que très doucement.

Les petites excitations ne provoquent pas de réactions, mais le pincement détermine des sauts énormes.

Conclusion : d'abord stade d'excitation léger, puis léger engourdissement.

Exp. 4.

16 juillet. Gren. poids : 67.1 gr.

10 h. 30. Inject. de 10 mgr. d'hydrchl. de bulbo-capn.

10 h. 35. Stade d'excitation, sauts etc.....

11 h. 15. Semble un peu aplatie.

12 h. 05. On parvient à écarter les pattes qui restent à certains moments dans la position d'abduction.

Les pattes sont peut être un peu plus flasques. Si l'on veut tourner la grenouille sur le dos, elle résiste, et fait des sauts violents. Fait des sauts à la suite de pincements.

¹⁾ PETERS Pharmacologische Untersuchungen über Corydalisalkaloide *Archiv für experimentelle Pathologie und Pharmakologie*, 1904, p. 157.

17 juillet : Paraît toujours un peu aplatie et engourdie, mais fait des sauts à la suite d'excitations.

Conclusion : Engourdissement, pas de vraie catalepsie. Peut faire des sauts.

Exp. 5.

17 juillet. Gren. poids 74.36 gr.

10 h. 10. Injection de 20 mgr. d'hydrochl. de bulboc.

10 h. 15. Excitation.

10 h. 30. Plus inerte, mais l'écartement de la patte donne lieu à une réaction excessivement brusque.

11 h. 22. Réactions moins violentes quand on écarte les cuisses. Réflexes vifs.

14 h. 30. Même état, l'animal est vigoureux.

Conclusions : pas d'effet pour 20 mgr.

Nous avons ensuite utilisé des doses très fortes.

Exp. 6.

18 juillet.

10 h. 10. Injection de 40 mgr. d'hydrchl. de bulboc.

10 h. 30. Secousses musculaires tétaniformes généralisées. L'animal est en hyper-extension.

10 h. 40. Encore quelques secousses, puis mort.

D'autres expériences ont été exécutées pour contrôler les expériences ci dessus, et nous ont donné les mêmes résultats.

Nous avons également étudié l'action de la bulbocapnine sur les réflexes de la grenouille. La grenouille était suspendue en position verticale et les réflexes du membre inférieur (obtenus par pincement ou par HCl. dilué) ont été étudiés et enregistrés graphiquement avant et après l'injection de bulbocapnine. Les réflexes sont toujours restés conservés, mais les réactions impulsives de l'animal qui étaient enregistrées en même temps étaient moins violentes après l'injection.

En résumé. Chez la grenouille les petites doses de bulbocapnine (2—3 milligrammes) n'ont pas d'effet. Les fortes doses (30, 40 mgr.) sont mortelles, et donnent lieu à des secousses superposables à celles que donne la strychnine, fait qui a déjà été noté par MODE ¹⁾.

Quant aux doses moyennes, (5—10 mgr.) elles donnent lieu semble-t-il, après un stade d'une certaine excitation, à un certain engourdissement, mais qui est différent de la catalepsie que donne la bulbocapnine chez d'autres animaux. Chez d'autres animaux en effet on peut obtenir, par certaines doses de bulbocapnine, un stade où l'animal se tient debout, mais est totalement immobilisé, et ne réagit plus à des excitations fortes (on peut par exemple dans ces conditions brûler les moustaches d'un chat sans qu'il change de place). Nous n'avons jamais pu observer de phénomène analogue chez la grenouille ; même lorsqu'elle paraît très engourdie, on peut provoquer par des excitations (pincement par ex.) des bonds et des sauts.

¹⁾ MODE Ueber die physiologischen Eigenschaften des Bulbocapninum hydrochloricum Thèse de Berlin 1892.

II.

Nous nous sommes ensuite attachés à l'étude de l'épreuve de la bulbocapnine chez les souris. Dans cette épreuve, comme dans toutes les expériences pharmacologiques la question des doses est capitale. Chez la souris, en particulier, qui nous a paru un animal très sensible, de faibles variations de doses donnent des résultats très différents.

Nous avons opéré sur 15 souris, pesant de 14.4 à 23 grs. Les doses de un à deux milligrammes d'hydrochlorate de bulbocapnine, injectées sous la peau du dos ou sous la queue, paraissent les plus efficaces pour réaliser une très belle catalepsie.

Catalepsie. En effet, environ 3 à 10 minutes après l'injection, l'animal parfois après un très léger stade de plus grande activité, commence à s'immobiliser, et se met un peu en boule. Au bout de 15 minutes environ, il est totalement immobile. On peut le pousser, l'exciter par des pincements, sans qu'il s'échappe. Il se tient sur ses pattes, les yeux ouverts. Si l'on prend alors la souris par la queue et qu'on l'approche d'un objet quelconque, elle s'y accroche immédiatement, et, si l'on y laisse, s'y maintient fixée pendant très longtemps. Même si l'on place l'animal dans une position difficile à garder, il s'y maintient. On voit par exemple dans la fig. 3 une souris enroulée autour d'un bec Bunsen avec une patte immobile en position verticale, et dans la fig. 4 deux souris dont l'une est placée debout, les pattes de devant appuyées et l'autre au sommet du bec. Nous avons laissé ainsi ces deux animaux fixés dans cette position pendant un quart d'heure, et nous les avons ensuite placés dans d'autres positions qu'elles gardaient de façon très prolongée. Nous avons pu par exemple laisser une souris suspendue par une patte antérieure, l'autre patte restant en l'air. L'animal se maintenait activement, et ne se laissait pas glisser. Il est absolument impossible d'ébaucher aucune de ces épreuves avec des souris normales qui s'échappent sans cesse, et sont d'une mobilité extrême.

La durée totale du stade de catalepsie est variable selon les doses, le poids et l'individualité des animaux. Il peut durer une à deux heures. (Fig. 5.)

Nous voulons souligner encore qu'il s'agit en pareil cas d'une vraie catalepsie. Ce qui est essentiel en effet c'est que l'animal exécute des contractions musculaires actives, nécessitant parfois des efforts considérables pour conserver la position, et pour maintenir l'équilibre dans des positions antigravifiques. Les réflexes d'équilibration sont d'ailleurs conservés avec cette dose : nous n'avons jamais pu mettre l'animal sur le dos sans qu'il se redresse immédiatement. Les yeux restent en outre parfaitement ouverts. Enfin l'animal peut montrer du négativisme passif et même parfois actif : c'est ainsi que, lorsqu'on le pousse en avant il résiste, et on ne peut le déplacer qu'en bloc. Parfois, il fait même en pareil cas quelques pas en arrière. Il ne s'agit donc pas, avec les doses que nous venons d'envisager, de narcose élective, comme le suppose M. DIVRY.

Par contre, si on emploie des doses plus élevées, en injectant par exemple quatre ou cinq milligrammes, on obtient un tableau tout à fait différent. La souris est alors aplatie contre la table, quelquefois la queue est redressée en l'air, l'animal est inerte, ferme les yeux ; il ne se tient pas fixé aux objets et se laisse glisser ; les réflexes d'équilibration sont supprimés et on peut le retourner sur le dos sans qu'il se redresse. On voit donc, qu'avec ces fortes doses, on ne peut guère parler de catalepsie vraie ; celle-ci existe quelquefois cependant, immédiatement après l'injection, mais elle est si fugace qu'elle passe facilement inaperçue.

Les fortes doses de bulbocapnine ne réalisent donc pas chez la souris, comme le font les petites doses, une catalepsie véritable ; elle déterminent plutôt un simple état d'engourdissement de toute l'activité de l'animal sans conservation des positions difficiles. D'après les photographies et les descriptions qu'il publie, il nous semble que c'est uniquement ce stade des doses élevées qu'a étudié M. DIVRY ¹⁾. Il qualifie cet état de narcose élective, et montre dans une de ses photographies une souris très aplatie sur le sol et la queue en l'air, comme dans l'intoxication par la morphine.

Pour la comparaison, nous avons pratiqué chez une souris des injections progressives de un, deux, trois milligrammes de morphine, et injecté jusqu'à deux centigrammes de cet alcaloïde. En contraste avec son extrême sensibilité pour la bulbocapnine, la souris supporte très bien des doses élevées de morphine (8 à 10 mgr.) sans modifications de son comportement. (Voir la fig. 6.)

Avec une injection de *deux centigr.* nous avons alors obtenu un véritable état de narcose : animal aplati, yeux clos, queue en l'air, immobilité totale. Mais en pareil cas, l'animal ne peut plus se tenir debout et se laisse tomber si on le place sur un objet. Il y a là une différence capitale avec la catalepsie. En effet, nous le répétons encore, la souris en pleine catalepsie bulbocapnique s'agrippe aux objets et se tient alors dans la position ainsi obtenue. A aucun point de vue, donc, la morphine ne réalise un syndrome comparable au syndrome si spécial que réalise la bulbocapnine.

Convulsions. Les doses élevées de bulbocapnine (4—5 mgr.) que nous venons d'envisager chez la souris, aboutissent en général à des crises convulsives le plus souvent mortelles. Ces crises surviennent quelquefois rapidement, 4 à 5 minutes après l'injection, immédiatement après le stade de torpeur. Ce sont d'abord des secousses isolées, puis bientôt des convulsions généralisées, accompagnées souvent d'émission d'urine, et d'écume à la bouche. Ces phénomènes épileptiques sont en général précipités par les

¹⁾ Il faut noter d'ailleurs que la bulbocapnine Merck, utilisée par M. DIVRY, qui est délivrée en ampoules contenant 0.1 gr. par centimètre cube, est en solution trop concentrée pour permettre l'emploi des doses de un à deux milligrammes susceptibles de réaliser le mieux la catalepsie chez un animal, aussi sensible que la souris. Nous avons d'ailleurs injecté à une souris quelques gouttes d'une ampoule de bulbocapnine Merck. L'animal ne présenta pas de vraie catalepsie, mais un court stade d'aplatissement suivi très rapidement de convulsions et de mort.

mouvements imprimés à l'animal, les secousses etc..... La mort est d'autant plus rapide que les convulsions sont plus intenses.

Hyperkinésies. Mais l'étude de la bulbo-capnine chez la souris met en évidence, non seulement la catalepsie, mais encore d'autres symptômes très intéressants : les *hyperkinésies*. Ces dernières manifestations toutefois sont loin d'être constantes et sont très variables. On ne peut les constater qu'en faisant de multiples expériences, et à des doses différentes. Elles sont d'ailleurs d'apparition brusque, inattendue et souvent très brèves.

Ces hyperkinésies peuvent revêtir différents aspects. Souvent il s'agit d'une agitation motrice brusque et violente : tout d'un coup l'animal fait des sauts, est projeté en l'air, se met à courir avec une vitesse extrême, parfois même saute de la table sur le sol. Une fois, nous avons vu l'animal décrire dans l'air un cercle complet, véritable „*looping the loop*” et tomber ensuite mort. Cette agitation saisit l'animal en pleine catalepsie, comme une sorte de raptus. Elle est très courte. Elle précède le plus souvent ou suit les convulsions, et est suivie de la mort à bref délai. Deux fois nous avons eu l'occasion de voir un stade intermédiaire entre la catalepsie et l'agitation motrice : l'animal étant en pleine catalepsie, si l'on le poussait un peu, on pouvait observer tout d'abord un peu de résistance, puis tout d'un coup l'animal faisait un grand bond sur la table, et retombait immédiatement en pleine catalepsie.

Ces hyperkinésies apparaissent surtout avec les doses élevées (4—5 mgr.) surtout si ces doses sont données en une fois. Il nous a semblé en effet qu'une même dose totale donnait souvent des résultats différents suivant qu'elle était administrée en une fois, ou d'une façon fractionnée. C'est ainsi, que, alors que la dose unique de 5 mgr. est en général mortelle, nous avons pu par des injections répétées de 2 mgr. d'heure en heure, injecter à trois souris des doses totales de 10 mgr. qui ne furent suivies que de torpeur, sans convulsions ni hyperkinésies, et sans évolution mortelle. Il semble donc que les *convulsions*, les *hyperkinésies*, soient surtout liées à une intoxication massive et brutale par la bulbo-capnine.

Bien qu'elles surviennent en général à la même période et dans les mêmes conditions, les hyperkinésies ne sauraient être identifiées et confondues avec les convulsions épileptiques ; leur aspect extérieur est bien différent : il s'agit de mouvements coordonnés, complexes, et très rapides, et non de simples secousses. Leur association avec l'épilepsie n'en est pas moins intéressante, elle pose le problème des rapports de certaines impulsions, et raptus moteurs avec le mal comitial, problème qui se pose parfois en clinique humaine à propos des impulsions et de l'agitation catatonique.

III. Conclusions.

„Les effets moteurs de la bulbo-capnine, écrit M. DIVRY, paraissent être „essentiellement les mêmes, que l'on s'adresse à un animal à sang froid, ou „à un animal à sang chaud. Il y a une simple différence de posologie dans „les deux cas.”

Nos expériences ne nous ont pas conduits à vérifier cette conclusion, et nous ont montré, au contraire, que l'effet de la bulbo-capnine était tout à fait différent chez la grenouille et chez la souris. Chez la grenouille, la bulbo-capnine ne donne pas de la catalepsie. Chez la souris, au contraire, la bulbo-capnine produit non seulement une catalepsie tout à fait caractéristique, à condition qu'on utilise une dose convenable, mais encore du négativisme, de la passivité, et mêmes certaines hyperkinésies. Ces hyperkinésies nous apparaissent très intéressantes ; nous les avons observées à la suite de la bulbo-capnine chez des animaux plus élevés, comme le singe ¹⁾. Elles posent le problème de leur étude comparative avec les impulsions, les raptus moteurs, et l'agitation catatonique chez l'homme que nous poursuivons actuellement.

Nous voulons rappeler encore, que pour toutes ces expériences, il est d'une importance capitale de doser avec beaucoup de précision et d'exactitude l'alcaloïde.

Notons enfin que les résultats différents obtenus chez la grenouille et la souris peuvent résulter de la constitution différente du système nerveux central de ces deux animaux. On sait en effet que la grenouille ne possède pas de néopallium, tandis que la souris en possède. Ces faits viennent confirmer l'importance du facteur cortical que nous avons déjà souligné dans la pathogénie de la catatonie.

¹⁾ DE JONG. Experimenteele en klinische catatonie. Nederl. Tijdsch. v. Geneesk., 1929, I, N^o. 6, p. 640—648.

L'un de nous (B) remercie vivement la Fondation ROCKEFELLER qui lui a donné la possibilité d'un séjour d'études à Amsterdam.

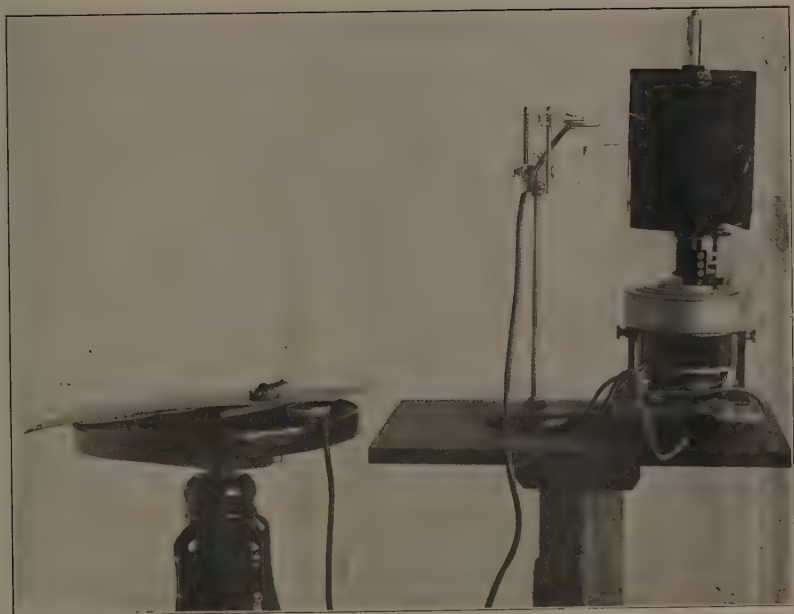


Fig. 1.
Dispositif permettant d'enregistrer l'immobilité naturelle de la grenouille.



Fig. 2. Les deux lignes supérieures indiquent l'immobilité de la grenouille normale.
Il n'y a qu'une seule interruption, causée par un tout petit déplacement de l'animal sur le carton.
La ligne inférieure indique le temps en secondes. Le kymographe tourne à très petite vitesse.



Fig. 3.
La souris garde la patte en l'air telle qu'on l'a placée contre le bec Bunsen.



Fig. 4.
Les animaux restent fixés dans les positions où on les a placés.



Fig. 5.

Fig. 5. Le chat et la souris cataleptiques.

Les deux animaux restent l'un à côté de l'autre sans bouger.
On soulève la tête du chat avec la main, l'animal en pleine catalepsie garde cette position.



Fig. 6.

Fig. 6. La fig. montre une souris injectée avec la bulbocapnine, immobile, les pattes antérieures reposant sur le rebord du bec Bunsen, et une autre souris, injectée avec la morphine, mobile, tournant en rond, et passant sous la souris précédente comme sous un tunnel.

Medicine. — *Etudes sur la catatonie expérimentale. II. L'épreuve de la bulbocapnine chez la poule. Catalepsie et sommeil.* Par H. BARUK (de Paris) et H. DE JONG (d'Amsterdam). (Communicated by Prof. B. BROUWER.) (Travail du laboratoire de physiologie de la clinique neurologique de l'Université d'Amsterdam.)

(Communicated at the meeting of September 28, 1929).

Dans un travail précédent nous avons étudié l'action de la bulbocapnine chez la grenouille et chez la souris, et montré que, si cet alcaloïde ne réalise pas la catalepsie chez la grenouille, il détermine chez la souris une catalepsie typique et en outre un certain nombre d'autres éléments du syndrome catatonique (négativisme, peut être même certaines hyperkinésies).

Nous avons d'autre part expérimenté l'action de la bulbocapnine chez la poule. Les résultats très spéciaux obtenus chez cet animal, notamment en ce qui concerne les rapports de la catalepsie et du sommeil nous ont incités à consacrer à ces expériences une publication spéciale.

Voici les protocoles de quelques unes de nos expériences.

Poule, poids : 1 kg. 900.

27 juillet.

10 h. injection sous la peau du dos de 0.040 gr. d'hydrochlorate de bulbocapnine.

10 h. 20. Rien d'anormal. L'animal va et vient, mange, vole, etc.

10 h. 25. L'animal commence à devenir immobile, ferme les yeux, tout en se tenant droit sur ses pattes. Au moindre bruit (toux, petit craquement etc.) l'animal rouvre les yeux, se redresse, mais se rendort dès qu'on le laisse au repos.

10 h. 30. Même aspect. L'animal dort debout sur ses deux pattes. On le réveille très facilement, et si on le stimule un peu, il saute, vole, etc. mais dès qu'on le laisse, il s'endort.

11 h. Même état.

Ainsi, dans cette expérience, la bulbocapnine réalise le tableau du sommeil tout à fait caractéristique (yeux fermés, réveil instantané au moindre bruit).

20. *Expérience le 29 juillet.*

Poule 1 Kg. 900.

10 h. 30 injection de 0.010 gr. d'hydrochlorate de bulbocapnine.

10 h. 45 commence à devenir immobile, le bec ouvert, respirations rapides et amples avec battements rythmés des crêtes (136 resp. par minute) ; on peut saisir l'animal maintenant sans difficulté.

11 h. s'affaïsse, ferme les yeux, bec très ouvert. Aspect du sommeil. Sursaute et se réveille au moindre bruit.

11 h. 15. L'animal est immobile debout sur ses pattes, les yeux ouverts. Ne réagit pas

aux excitations (pincements, secousses, etc.) On pousse l'animal en avant, il avance une patte, et reste ainsi immobile. (Voir la fig.)

On renouvelle la poussée, la poule fait un à deux pas en avant, résiste, puis fait un à deux pas arrière dès qu'on l'abandonne.

11 h. 25. L'immobilité semble s'atténuer. On ne peut plus saisir l'animal, il se débat, s'enfuit et s'envole. 84 respirations par minute.

11 h. 26. De nouveau, l'animal est complètement immobile. On le prend sans aucune difficulté. On le pousse en arrière, il résiste, recule sous la poussée de un ou deux pas, puis revient en avant.

L'animal cherche à s'isoler, dans les coins, ou sous les meubles.

Ainsi donc, dans l'expérience ci dessus, on note à la suite de l'injection de bulbocapnine, après une phase de sommeil, un état de catalepsie accompagné même d'un certain degré de négativisme. Mais, cette catalepsie est essentiellement *variable, transitoire* ; elle disparaît à certains moments, et reparait d'une minute à l'autre.

Nous avons cherché si l'on pouvait saisir les conditions qui favorisent les variations si curieuses de la catalepsie. Celle ci, semble surtout marquée en l'absence de stimulations extérieures, et peut être suspendue par des incitations, comme le montre l'expérience suivante :

Exp. 3. Poule 1 Kg. 900.

14 h. Poule injectée le matin ; un peu engourdie.

14 h. 20. Injection de 0.007 gr. d'hydrochl. de bulbocapnine.

14 h. 45. S'asseoit, la tête tombe en avant, les yeux se ferment. Mais se réveille au moindre bruit.

15 h. 10. Nouvelle injection de 0.003 gr. d'hydrochl. de bulbocapnine.

15 h. 20. Catalepsie : immobilité ; pas de réaction quand on saisit l'animal. Conserve les positions : on porte successivement la tête en haut, en bas, latéralement, garde ces diverses positions. On transporte alors l'animal complètement inerte dans la pièce voisine pour le photographe. A peine le pose-t-on sur la table, la catalepsie cesse soudain, la poule s'enfuit.

15 h. 30. Nouvelle injection de 0.007 gr. d'hydrochl. de bulboc.

15 h. 45. Catalepsie marquée ; immobilité totale. Aucune réaction lorsqu'on la prend, ou l'excite.

Tout d'un coup, la porte est ouverte à grand bruit. L'animal se redresse, saute, et s'envole de la table sur le radiateur, reste éveillé, remuant, et sautillant.

16 h. Animal tout à fait normal — va et vient — saute.

On ferme alors la pièce, après avoir réalisé l'obscurité. On laisse ainsi l'animal dans le silence absolu.

16 h. 10. Catalepsie marquée — on la pousse en bloc. Aucun mouvement spontané.

18 h. 30. Nouvelle injection de 0.040.

18 h. 35. Ouvre le bec, respirations rapides (120 p. min.) battements des crêtes — les yeux restent ouverts.

Le lendemain, l'animal paraît normal, un peu engourdi toutefois.

Ainsi, tandis que le simple fait de transporter la poule d'une pièce dans une autre, fait disparaître la catalepsie, celle ci reparait en laissant l'animal dans le silence et l'obscurité.

Nous avons enfin expérimenté l'action des très fortes doses.

Exp. 4.

31 juillet.

15.15 injection de 0.075 gr. d'hydrochl. de bulbocapnine.

15 h. 22 commence à s'immobiliser, ouvre le bec.

15 h. 25. catalepsie — on pousse l'animal en bloc.

15 h. 30. nouvelle injection de 0.075 gr.

15 h. 33. Animal complètement affaissé, repose sur le ventre, ne peut faire aucun mouvement, ni se tenir debout — bec ouvert — respirations extrêmement rapides (200 p. min.) salivation très accentuée. Si on retourne toutefois la poule sur le dos, elle se redresse aussitôt.

Le lendemain, l'animal se tient debout, mais est engourdi. Il se remet peu à peu.

Ainsi les très fortes doses ont réalisé, non plus la catalepsie, mais une véritable paralysie, transitoire d'ailleurs.

Conclusions.

Les expériences précédentes nous montrent donc que l'injection de bulbocapnine chez la poule à des doses moyennes (entre 10 et 40 mgr. environ) est susceptible de déterminer deux états différents, d'une part du sommeil typique, d'autre part de la catalepsie :

Ces deux états se distinguent par les caractères différentiels suivants : dans le sommeil, l'animal a les yeux fermés, il est souvent un peu affaissé, enfin et surtout il se *réveille instantanément et complètement* au moindre bruit ou à la moindre excitation, pour retomber ensuite dans le sommeil dès qu'on l'abandonne au repos.

Dans la catalepsie, au contraire l'animal se tient debout, les yeux ouverts, immobile. Le bruit, les incitations légères ne modifient pas son état. D'autre part, il présente une passivité particulière en vertu de laquelle on peut le pousser en avant, en arrière, un peu comme un jouet mécanique. Ces caractères différentiels entre le sommeil et la catalepsie que nous venons de signaler chez l'animal intoxiqué par la bulbocapnine, sont exactement les mêmes que ceux que l'on observe respectivement dans les mêmes syndromes en pathologie humaine et sur lesquels l'un de nous a insisté avec le Pr CLAUDE ¹⁾.

Il importe toutefois de faire remarquer que, malgré les différences que nous venons de souligner entre le sommeil pathologique et la catalepsie, ces deux manifestations se trouvent, dans les expériences que nous venons de rapporter, étroitement associées. On voit en effet chez la poule intoxiquée alterner le sommeil pathologique et la catalepsie. D'autre part la catalepsie chez la poule peut dans une certaine mesure être influencée par les stimulations extérieures. C'est ainsi qu'elle disparaît en déplaçant l'animal ou en l'excitant d'une façon prolongée. Ces faits sont à rapprocher de la

¹⁾ H. CLAUDE et H. BARUK. Les crises de Catalepsie. Diagnostic avec le sommeil pathologique. Leurs rapports avec l'hystérie et la catatonie. Encéphale Mai 1928.

suspension possible de la catalepsie chez l'homme sous l'influence de diversions psychiques, comme nous avons pu l'objectiver à plusieurs reprises. Ces faits permettent donc de penser que les mécanismes physiologiques de la catalepsie et du sommeil sont peut être assez voisins. On sait d'ailleurs que PAVLOV ¹⁾ considère la catalepsie et l'état hypnotique comme une manifestation intermédiaire entre le sommeil et l'état de veille, et comme due à une inhibition limitée exclusivement au cortex, et non diffusée aux centres basilaires. Il n'y aurait donc qu'une question de degré et de différence d'étendue de l'inhibition entre la catalepsie et le sommeil pathologique.

Un autre caractère sur lequel nous désirons insister, consiste dans les variations extrêmes de la catalepsie bulbocapnique chez la poule. Nous avons vu que cette catalepsie peut disparaître d'une minute à l'autre. Ce fait est à rapprocher également des variations si capricieuses et souvent si brusques des manifestations du syndrome catatonique chez l'homme.

Enfin, la bulbocapnine réalise chez la poule, surtout à doses élevées, des troubles végétatifs importants : polypnée, salivation très accentuée. Ces troubles végétatifs que nous avons retrouvés dans l'action de la bulbocapnine chez d'autres animaux constituent également une analogie de plus avec les troubles analogues de la catatonie humaine ²⁾.

¹⁾ I. P. PAVLOV. Conditioned reflexes. Oxford 1927, pages 265 et 266.

²⁾ L'un de nous (B.) remercie vivement la Fondation ROCKEFELLER qui lui a donné la possibilité d'un séjour d'études à Amsterdam.

H. BARUK et H. DE JONG: ETUDES SUR LA CATATONIE EXPÉRI-
MENTALE. II. L'ÉPREUVE DE LA BULBOCAPNINE CHEZ LA POULE.
CATALEPSIE ET SOMMEIL.



On peut saisir la poule avec la main sans qu'elle s'enfuie
comme le ferait une poule normale. Elle résiste à la poussée.

Chemistry. — *Die Pseudo-komponenten des Wasserstoffs.* II. Von Prof. A. SMITS. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of September 28, 1929).

Seit der Publikation meiner Mitteilung in der Physikalischen Zeitschrift XXX 1929 (Eingegangen 29 März 1929) und meiner Abhandlung in den Proceedings Kon. Akad. v. Wet. 32, 603, 1929, sind von BONHOEFFER und HARTECK sowie von EUCKEN und HILLER ausführliche Abhandlungen über Para- und Ortho Wasserstoff und ihre Umwandlung in der Zeitschr. f. phys. Chemie Abt. B. 4, 113 und 142 (1929) erschienen. In demselben Heft dieser Zeitschrift publizierten CLUSIUS und HILLER ihre Untersuchungen über die spezifischen Wärmen des Parawasserstoffs in festen, flüssigen und gasförmigen Zuständen. [Z. f. phys. Chemie Abt. B. 4, 158 (1929).]

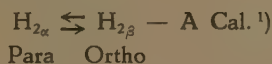
Diese Abhandlungen veranlassen mich in Anschluss an die von mir schon gegebenen Betrachtungen noch einige Bemerkungen zu machen.

Es hat sich herausgestellt, dass Wasserstoff aus zwei Molekülarten besteht, welche, wie die Theorie der Allotropie aussagt, als die Pseudokomponenten des Wasserstoffs zu betrachten sind.

Hieraus folgt, dass, wenn sich der Wasserstoff unär verhält, diese Pseudokomponenten miteinander in innerem Gleichgewicht sind, oder dass man mit einem *Nicht-gleichgewichts-zustande* arbeitet, welcher nur eine der Pseudokomponenten enthält.

Aus Versuchen betreffend Wärmeleitfähigkeit und spezifische Wärme lässt sich schliessen, dass das innere Gleichgewicht sich bei Anwendung eines geeigneten Katalysators ziemlich rasch einstellt.

In Uebereinstimmung mit dem Zeichen der Reaktionswärme verschiebt sich das innere Gleichgewicht.¹⁾



bei Temperaturerhöhung nach der β (Ortho)-Seite.

Bei 20,93° abs. liegt das innere Gleichgewicht, welches sich unter den katalytischen Einfluss von Kohle rasch einstellt bei 99,7 % α und 0,3 % β und bei 85° abs. liegt es bei 48 % α und 52 % β .

Die zwei Molekülarten α und β kommen aber in verschiedenen Rota-

¹⁾ Unter innerem Gleichgewicht verstehen wir das Gleichgewicht zwischen den verschiedenen Molekülarten desselben Stoffes.

tionszuständen vor; nennen wir die Grundzustände von α und β , α_0 und β_1 so existieren von α auch noch die Rotationszustände α_2, α_4 u.s.w. und von β noch die Rotationszustände β_3, β_5 u.s.w. und je höher die Temperatur um so mehr treten die höheren Rotationszustände auf. Die hier oben angegebenen Zusammensetzungen beziehen sich auf die *totalen* Mengen α und β .

Während die *totale* Umwandlungsenergie A in obenstehender Gleichung eine verwickelte Temperaturfunktion ist, muss die Energieänderung bei der Umwandlung des α -Grundzustandes in den β -Grundzustand unabhängig von der Temperatur sein.

Die Grosse B in der Gleichung (2)



ist also *nicht* eine Temperaturfunktion.

Für das innere Gleichgewicht zwischen den Grundzuständen folgt also nach der Formel

$$\ln K_{Gr} = -\frac{Q}{RT} + C \quad (3)$$

dass $(\ln K_{Gr})_{T=\infty} = C$, welcher Wert übereinstimmen muss mit dem Werte für $\ln \frac{p_{\beta_1}}{p_{\alpha_0}}$ in der BOLTZMANNschen Gleichung

$$\frac{N_{\beta_1}}{N_{\alpha_0}} = \frac{p_{\beta_1}}{p_{\alpha_0}} e^{-\frac{Q}{RT}} \quad (4)$$

wenn $\frac{N_{\beta_1}}{N_{\alpha_0}}$ das Verhältnis zwischen den β und α Molekülarten in dem Grundzustande und $\frac{p_{\beta_1}}{p_{\alpha_0}}$ das Verhältnis der Phasenausbreitungen oder statistische Gewichte dieser Molekülarten darstellt.

Aus spektroskopischen Messungen von HORI¹⁾ hat BEUTLER²⁾ $Q (= -B)$ zu 329 Cal. berechnet und aus den statistischen Gewichte folgt weiter, dass K_{Gr} bei $T = \infty$ den Wert 9 haben wird, sodass $C = 2,196$.

Es sei hier ausdrücklich auf das Resultat hingewiesen dass also

$$(K_{Gr})_{T=\infty} = 9.$$

Wir sind also jetzt im Stande den Wert von K_{Gr} für verschiedene Temperaturen zu berechnen.

Weil die zwei Molekülarten, jede für sich, noch in verschiedenen Rotationszuständen vorkommen, und weil das Verhältnis zwischen diesen Rotationszuständen sich mit der Temperatur ändert, ist die Energieänderung der *totalen* Umwandlung, welche in Gleichung (1) mit A angegeben worden ist, eine Temperaturfunktion und sind die vorange-

¹⁾ Z. f. Phys. **44**, 834 (1927).

²⁾ Z. f. Phys. **50**, 585 (1928).

henden Überlegungen hier nicht mehr zutreffend. An der Stelle der gegebenen Gleichung (3) bekommt man nun für $\ln K$ eine mehr verwickelte Beziehung.

Die statistische Betrachtungen welche hier notwendig herangezogen werden müssen, zeigen, dass das Verhältnis $\frac{\sum p_\beta}{\sum p_\alpha}$ für alle Rotationszustände von α und β zusammen, $= 3$ ist, sodass die Konstante des *totalen* innerlichen Gleichgewichts dann bei T_∞ den Wert 3 hat.

Also

$$(K_{tot})_{T=\infty} = 3.$$

In der nächsten Mitteilung wird der Verlauf von K_{Gr} und K mit der Temperatur näher betrachtet werden.¹⁾

Das System Wasserstoff bietet uns zwei Vorteile. Erstens ist es ein Vorteil, dass das innere Gleichgewicht in der Gasphase bei 20,93° abs. bei 99,7 % α (Para) liegt, was BONHOEFFER und HARTECK in die Lage setzte auf einfache Weise, unter den katalytischen Einfluss von Kohle, die α -Pseudo-komponente in beinahe vollkommen reinem Zustand darzustellen. Zweitens ist es ein Vorteil, dass ohne Katalysator und bei relativ niedrigem Druck das innere Gleichgewicht sich bei nicht zu hohen Temperaturen nur sehr langsam einstellt, so dass man dadurch im Stande ist etwas über das Pseudo-binäre System zu erfahren.

Man hat aber nicht genug darauf geachtet, dass man unter diesen Umständen, ohne Katalysatoren und also nicht einen inneren Gleichgewichtszustand abwartend, mit Mischungen und nicht mit inneren Gleichgewichtszuständen, welche sich unär verhalten, arbeitet.

Gewöhnlicher Wasserstoff ist eine solche Mischung ausser innerem Gleichgewicht und man kann deshalb nicht von dem *Siedepunkte*, *Schmelzpunkte* und *Tripelpunkte* des gewöhnlichen Wasserstoffs sprechen, ebenso wenig, wie man das von flüssiger Luft tun kann. Gewöhnlicher Wasserstoff, ebenso wie alle anderen Mischungen von α - und β -Wasserstoff, besitzt einen *Siedetrajekt*, und einen *Schmelztrajekt*, sowohl unter höherem Druck, wie unter Dampfdruck²⁾. Man kann hier nur sprechen von einem *Anfangs-* resp. *End-Siedepunkt* und *Anfangs-* resp. *End-Schmelzpunkt*, womit dann gemeint ist die Temperatur, bei welcher bei sehr kleinem Dampfvolum das Sieden oder das Schmelzen anfängt. resp. beendet ist. Das sind für jede Zusammensetzung bestimmte Grössen.

¹⁾ Es wird interessant sein den gewöhnlichen Wasserstoff, auf verschiedene Weisen bereitet¹⁾ näher zu studieren.

²⁾ Es leuchtet ein, dass gewöhnlicher Wasserstoff, welchen man längere Zeit bei z. B. -190° aufbewahrt hat, diese Trajekte zeigen wird, weil, wenn nicht ein kräftiger Katalysator anwesend ist, das innere Gleichgewicht sich während der Schmelzung oder des Siedens nicht einstellen kann.

Die Resultate von GIAUQUE und JOHNSTON (J. Amer. Chem. Soc. 50, 3221 (1928), mit ihrem speziellen Wasserstoff erhalten, welche aber von Ihnen, meiner Einsicht nach, nicht richtig gedeutet sind, weisen sehr deutlich in dieser Richtung.

Die Siedetrajekte und speziell die Schmelztrajekte sind hier zwar klein, aber die Trajekte sind essentiell dem Wasserstoff und nicht den Verunreinigungen zu zuschreiben.

Im ganzen Pseudo-binären System¹⁾ kann man nur in den zwei Grenzfällen von einem Siedepunkt, Schmelzpunkt, Tripelpunkt sprechen, nämlich wenn man mit reinem α -(Para) oder reinem β -(Ortho) Wasserstoff oder m.a.W. mit den reinen Pseudo-komponenten arbeitet.

Es ist natürlich von grosser Bedeutung, wie ich schon früher bemerkte, das Pseudo-binäre System des Wasserstoffs genau kennen zu lernen. Und in diesem Pseudo-binären System liegt das unäre System des Wasserstoffs, welches sich nur finden lässt, wenn man dafür Sorge trägt, dass unter Anwendung geeigneter Katalysatoren das innere Gleichgewicht bei dem Experiment eingestellt bleibt. Unter diesen Umständen lässt sich dann u. A. die Dampfspannungskurve des festen und des flüssigen Wasserstoffs, in innerem Gleichgewicht, und somit der Siedepunkt und der Tripelpunkt des unären Wasserstoffs bestimmen.

Es ist eben dieser Wasserstoff in innerem Gleichgewicht, welchen wir fast noch gar nicht kennen.

BONHOEFFER und HARTECK fanden für den Dampfdruck der α (para), Pseudokomponente bei 20.39° den Wert 787 mm Hg. Setzen wir nun voraus, dass der *Anfangs-Siedepunkt* des gewöhnlichen Wasserstoffs, der eine Mischung von 25 % α (Para) und 75 % β (Ortho) ist, nicht viel von 20.39° , dem in der Litteratur angegebenen Siedepunkte des gewöhnlichen Wasserstoffs abweicht, dann können wir sagen, dass der *Anfangsdampfdruck* bei 20.39° wenig von 760 mm Hg verschieden sein muss. BONHOEFFER und HARTECK fanden, dass ein Gemisch von 80.5 % α (Para) bei 20.39° einen Dampfdruck von 781 mm Hg besitzt; nehmen wir nun wieder an, dass der *Anfangsdampfdruck* dieser Mischung nicht viel von 781 mm Hg abweicht, so bekommen wir folgende Zahlen.:

| Zusammensetzung des Gemisches. | Anfangsdampfdruck bei 20.39° abs. |
|--------------------------------|--|
| 100 % Para | 787 mm Hg |
| 80.5 % „ | ± 781 mm Hg |
| 25 % „ | ± 760 mm Hg |

Aus diesen Zahlen folgt, dass wie BONHOEFFER und HARTECK schon bemerkten, der Dampfdruck praktisch linear von der Zusammensetzung der flüssigen Phase abhängt. Für den Dampfdruck von β (Ortho) findet

¹⁾ Das System Wasserstoff verhält sich binär, wenn sich das innere Gleichgewicht *nicht* eingestellt hat und deshalb heisst das System dann Pseudo-binär.

man dann 751 mm Hg. Die PX -Fig. des Pseudo-binären Systems wird nun bei 20.39° abs. folgende sein: (siehe Fig. 1).

Die obere Flüssigkeitskurve wird also praktisch eine Gerade sein, aber, auch wenn sie absolut eine Gerade ist, wird die Dampfkurve, wie bekannt,

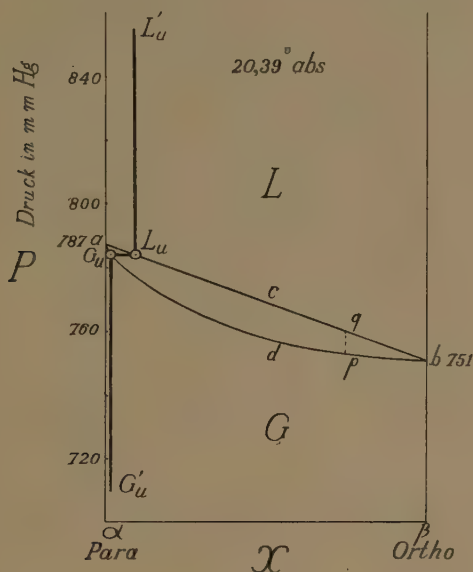


Fig. 1.

eine Hyperbel sein mit den Koordinatenachsen als Asymptoten.

Der Dampfdrucktrajekt bei der Kondensation von einer Mischung von 25 % Para und 75 % Ortho ist also durch die Entfernung pq gegeben. Bei unendlich kleiner Flüssigkeitsmenge ist der Dampfdruck angegeben durch p und bei unendlich kleiner Dampfmenge durch q . Dieser Dampfdrucktrajekt wird klein sein, doch sicherlich messbar. Der Wert 760 mm Hg soll zwischen p und q gelegen sein.¹⁾

In dieser P, X -Figur liegt nun die P, X -Figur des unären Systems, d. h. des Wasserstoffs in innerem Gleichgewicht. Wir wissen aber leider nicht, wie hoch bei 20.39° der Dampfdruck des Wasserstoffs in innerem Gleichgewicht und ebenso wenig wie die Zusammensetzung der koexistierenden Phasen unter diesen Umständen ist.

Weil aber BONHOEFFER und HARTECK fanden, dass bei 20.39° unter dem katalytischen Einfluss vom Kohle, Wasserstoff sich in einem Gemisch von 99.7 % α (Para) Wasserstoff verwandelt, kann der Dampfdruck des Wasserstoffs in innerem Gleichgewicht bei 20.39° durch die Linie $G_u L_u$

¹⁾ Diese Figur lässt erwarten, dass die beiden Pseudokomponenten durch fraktionierte Destillation eines Gemisches erhalten werden können.

angegeben werden, und die koexistierenden Dampf- und Flüssigkeits-Phasen sind also in G_u resp. in L_u gelegen und dabei soll G_u stark an der α -Seite liegen.

Diese zwei Punkte geben also das *unäre* Gleichgewicht zwischen Dampf und Flüssigkeit an, d.h. das zwei-Phasen Gleichgewicht Dampf + Flüssigkeit, wenn beide Phasen in innerem Gleichgewicht sind und das System sich deshalb wie ein *einkomponentiges* System verhält.

Von G_u aus geht die Linie $G_u G'_u$, welche die Lage der inneren Gleichgewichte in der Gasphase bei niedrigerem Druck angibt und von L_u aus geht die Linie $L_u L'_u$ für die inneren Gleichgewichte in der flüssigen Phase bei höheren Drucken. Beide Linien sind vertikal gezeichnet, weil der Druck auch auf das innere Gleichgewicht in der flüssigen Phase wahrscheinlich praktisch keinen Einfluss haben wird.

In Zusammenhang mit dieser $P.X$ -Figur können wir nun auch die $T.X$ -Figur, oder die Siedefigur des Pseudo-binären Systems bei 1 Atm. Druck, und ebenso die wahrscheinliche Lage der unären Figur in diesem Pseudobinären System angeben.

Wir bekommen dann Fig. 2.

Die Flüssigkeitslinie $a c b$ ist praktisch eine Gerade; a_1 , der Siedepunkt

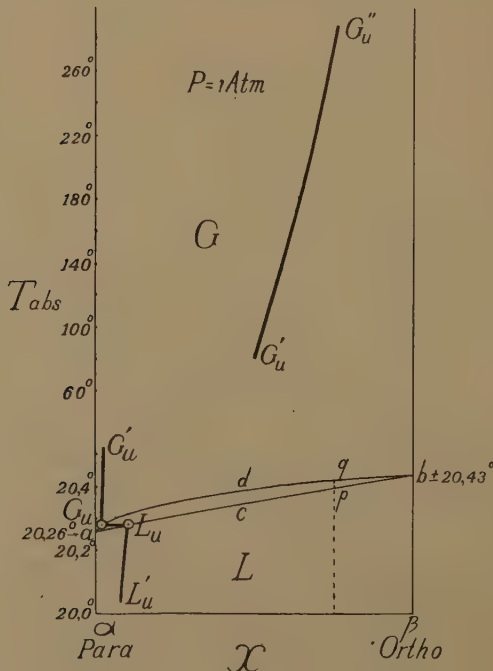


Fig. 2.

von αH_2 , liegt bei 20.26° , und wenn wir nun annehmen, dass 20.39° der Anfangs-Siedepunkt des gewöhnlichen Wasserstoffs ist, dann liegt der Siedepunkt von βH_2 bei 20.43° .

Die Dampflinie $a d b$ ist eine Hyperbel. Der Siedetrajekt des gewöhnlichen Wasserstoffs ist hier wieder durch die Entfernung $p q$ angegeben und p ist der Anfangs-Siedepunkt.

Die Lage der unären $T. X$ -Figur ist nun leicht in groben Zügen in dieser Pseudo-binären Fig. anzugeben, wenn wir nämlich bedenken, dass das innere Gleichgewicht in der Gasphase bei $\pm 20.93^\circ$ bei ungefähr 99.7% a liegt, bei 83° bei ungefähr 50% a und bei 290° wahrscheinlich nicht weit von 25% a entfernt ist. Die inneren Gleichgewichte in der Gasphase können also dargestellt werden durch die Linie $G''_u G_u$, von welcher hier ein Zwischenteil fortgelassen ist, weil die Fig. sonst zu gross würde. — Dort, wo diese Linie die Pseudo-binäre Figur begegnet, liegt die Dampfphase G_u des unären Siedegleichgewichts, und die koexistierende flüssige Phase, welche ebenfalls in innerem Gleichgewicht ist, liegt in L_u . Die inneren Gleichgewichte in der Flüssigkeit unterhalb des Siedegleichgewichts sind angegeben durch die Linie $L_u L'_u$. Während also gewöhnlicher Wasserstoff bei p anfängt zu siedend, liegt das unäre Siedegleichgewicht, welches unabhängig von den relativen Mengen von Flüssigkeit und Dampf ist, niedriger.

Aber dieses unäre Siedegleichgewicht ist natürlich nur bei Anwendung eines stark wirkenden Katalysators zu realisieren.

Wie steht es nun mit der Schmelz-Figur?

BONHOEFFER und HARTECK neigen dazu anzunehmen, dass auch der „Schmelzpunkt“ linear von der Konzentration der beiden Pseudokomponenten abhängt. Ob dieses wirklich so ist, d.h. ob man das von dem Anfangsschmelzpunkte sagen kann, wissen wir noch nicht. Die Hauptsache ist aber jetzt zu wissen, ob diese Änderung des Anfang-Schmelzpunktes mit der Konzentration *kontinuierlich* ist. Das ist nämlich eine sehr interessante Frage, denn wenn diese Änderung kontinuierlich ist, dann steht es fest, dass die zwei Pseudokomponenten des Wasserstoffs eine *kontinuierliche* Reihe Mischkristalle bilden.

Ich erachtete dieses sehr wahrscheinlich und ich habe deshalb in meiner früheren Abhandlung an der ersten Stelle diese Möglichkeit erwähnt.

Obwohl wir noch keine Sicherheit, sondern nur Wahrscheinlichkeit besitzen, will ich eine kontinuierliche Mischkristallreihe voraussetzen und die Projektion der Dreiphasen-Gleichgewichte auf die $T. X$. Ebene des Pseudo-binären Systems nochmals betrachten, weil die Lagen der Projektion der Zwei-phasen Gleichgewichte des unären Systems und der Zusammenhang des unären mit dem Pseudo-binären System jetzt, was die Zusammensetzungen anbelangt, weniger schematisch angegeben werden können.

In Fig. 3 ist $a c b$ die Flüssigkeitslinie, $a d b$ die Dampflinie und $a e b$ die Mischkristall-linie der Dreiphasenkoexistenz $S + L + G$ im Pseudo-binären System.

nicht auf Wasserstoff im inneren Gleichgewicht bezieht, sodass dieses auch für den Wert für den kritischen Druck $P_{KH_2} = 12.8$ atm. gilt.

Das zweite Linienpaar $G_u G_u$ und $S_u S_u$ gibt die Koexistenz zwischen den Gasphasen und den Mischkristallphasen in innerem Gleichgewicht (Sublimationslinie) unterhalb des Dreiphasen-gleichgewichts $G_u L_u S_u$ an.

Das Dreiphasen-Gleichgewicht $G_u L_u S_u$ ist also das Gleichgewicht, das sich beim Schmelzpunkt unter dem Dampfdruck beim unären Verhalten einstellt. In der $P \cdot T$ -Figur, welche wir jetzt noch näher besprechen müssen, fallen diese Punkte $G_u L_u S_u$ in einem Punkt zusammen, weil die verschiedenen Zusammensetzungen dort nicht zur Äusserung gelangen. Das unäre Dreiphasengleichgewicht ist dort ein *Tripelpunkt*.

In der Voraussetzung, dass der Beginn-Schmelzpunkt unter den Dampfdruck sich kontinuierlich mit der Zusammensetzung ändert, wollen wir auch die $P \cdot T$ -Figur, welche ich in meiner ersten Mitteilung schon in grossen Zügen angab, näher betrachten.

Die Tripelpunkte der Pseudo-komponenten α und β sind angegeben

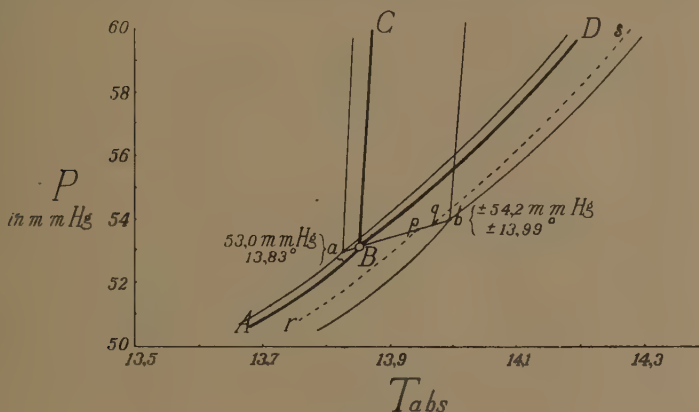


Fig. 4.

durch a und b . a liegt bei 13.83° abs. und 53.0 mm Hg und b wird bei $\pm 13.99^\circ$ abs. und ± 54.2 mm Hg liegen, wenn die Linie ab , welche die Dreiphasenlinie für $S + L + G$ vorstellt, praktisch eine Gerade ist. Die Linien rp und qs geben die Dampfdrucklinien des festen und des flüssigen gewöhnlichen Wasserstoffs bei einem bestimmten Volum an. Ist das Dampfvolum, wenn man der Schmelzpunkt unter dem Dampfdruck der Mischung 75% Ortho bestimmte, zufälliger Weise sehr klein gewesen, und hat man den Anfang der Schmelzung beobachtet, dann werden die Zahlen 13.95° abs. und 53.9 mm Hg sich auf den Punkt p , oder den *Anfangs-schmelzpunkt* unter dem Dampfdruck beziehen. pq ist dann ein kleiner Teil der Dreiphasenlinie, welchen man hatte beobachten können.

Der Tripelpunkt des Wasserstoffs in innerem Gleichgewicht B wird sehr dicht bei dem Punkte a liegen und die unäre $P. T$ -Figur wird also gegeben durch die drei Linien AB (Sublimationslinie), BC (Schmelzlinie) und BD (Dampfspannungslinie der Flüssigkeit), von welcher die letzte natürlich dort endet, wo sie die kritische Kurve des Pseudo-Systems begegnet, d.h. in dem unären kritischen Punkt. In der $T. X$ -Projektion geht die kritische Kurve durch das Maximum der kontinuierlichen Dampf-Flüssigkeit-Schlinge des unären Systems. Weitere Besonderheiten findet man in „Die Theorie der Allotropie.“

Schliesslich will ich noch bemerken, dass, wie Fig. 3 wahrscheinlich macht, der feste Wasserstoff in innerem Gleichgewicht eine Mischkristallphase sein wird, welche sehr reich an α (Para) ist und deshalb in *Zusammensetzung* stark vom gewöhnlichen, festen Wasserstoff abweichen wird.

Laboratorium voor Algemeene en
Amsterdam, 18 Sept. 1929. Anorganische Chemie der Universiteit

Neurology. — *Some Clinical and Anatomical Observations on the "Paraplegie en Flexion" and Related Motor Disturbances.* By Dr. W. J. C. VERHAART. (From the Laboratory in the Mental Hospital "Oud Rosenburg", The Hague.) (Communicated by Prof. B. BROUWER.)

(Communicated at the meeting of September 28, 1929).

The researches made into this paraplegia, covering the last 30 years did not result in showing a clear anatomical localisation, since the post mortem examinations of the greater part of the cases showed degenerations in nearly all parts of the central nervous system.

A short historical outline of the subject under discussion will prove this assertion.

In 1911 BABINSKI ascertained that in this paraplegia the patellar and Achilles jerks were not increased, while the reflexes "dits de défense", the reflexes of flexion of the leg obtained by stimulation of the foot were always present. BABINSKI noticed this dissociation of reflexes in cases of compression of the spinal cord, of the Pons, and in some cases of Sclerosis Multiplex, and admitted that it was possible that this phenomenon was caused by cerebral lesions.

Cases of paraplegia in flexion of central origin were described by MARIE and FOIX in 1920, by ALAJOUANINE in 1923, by WILLIAM HERMAN in 1926, by R. LEY and LUDO V. BOGAERT in the same year. These researchers noticed multiple degenerations and foci in the cortex, in the marrow of the hemispheres, and in the basal ganglia, as well as in the cord in some cases. Especially the region of the paracentral gyrus of both sides was affected, more or less complete degeneration of the pyramidal tracts was always to be found. The symptoms of this paralysis were only found in patients suffering from organic dementia.

A circumscribed anatomical substratum could not be given. ALAJOUANINE, however, was struck by the frequency of bilateral lesion of the paracentral region, where the cortical centrum of the motility of the lower limbs must be supposed to be located. He is of opinion that this bilateral lesion is the cause of paralysis in flexion of the lower limbs. The same view is held by R. LEY and LUDO V. BOGAERT.

In 1928 I published a case of paraplegia in flexion, in which many lacunae were found in the cortex and basal ganglia, as well as a considerable loss of ganglion-cells in the frontal and the central gyri. There was a marked loss of fibres in both pyramidal and fronto-pontine tracts, the mid-brain and the lower parts of the nervous system showed no primary

degenerations. I, therefore, thought that the combination of frontal and central lesions were the cause of the paralysis in flexion of the lower limbs.

Also in German publications similar cases are to be found, although they are not described there as instances of paraplegia in flexion. JACOB, STIEF, KASHIDA, O. FÖRSTER and KIRSCHBAUM describe cases of Arterio-sclerosis cerebri, "spastische Pseudosclerose", and other diseases, which led to paralysis in flexion of the lower limbs. Foci were found in most parts of the nervous system, degeneration of the pyramidal tracts nearly always occurred to a greater or smaller extent.

In the mental hospitals, where patients with disseminated cerebral lesions will frequently have to come, symptoms of paralysis in flexion of the legs are rather common, which enabled me to observe a small number of such patients in a comparatively short time, in each case checking the conclusions made by means of a post mortem examination. When examining more closely the symptoms of motor disturbances, it soon became obvious that there existed great differences between the symptoms of the various patients, and that a classical "Paraplegie en flexion" was only present in some of them.

Clinically the patients must, therefore, be divided into 3 groups, the first of the three being the pure "paraplegie en flexion", with both legs paralysed in flexion. The second group consists of patients suffering from a *hemiplegia* with flexed lower limb, without motor disturbances of the contralateral arm and leg. The third group was formed by patients with both legs in flexion, who, when examined clinically, were found to have absolutely no signs of paralysis, being able to stretch their legs actively, and to make all other movements without help. Notwithstanding this, they were always found with their legs sharply flexed. The reflexes "dits de défense" were increased.

The first patient to be described suffered from a paraplegia in flexion during the last year of his life. He passed the last 6 years of his life at Oud Rosenburg and other hospitals because of his general paralysis. Specific treatment, Recurrens and Malaria could not arrest a steady mental and physical decay. During the last months of his life he could hardly speak any more, both his legs were constantly flexed, while he was unable to change this attitude. No mention is made of his reflexes.

A histological examination made after death confirmed the diagnosis. Macroscopically the brain showed a marked atrophy of the windings, the frontal and temporal pole were extremely atrophied the other windings of these lobes were also atrophied, though to a smaller degree, except the back of the middle frontal gyrus. The frontal operculum of both sides was atrophied, as well as the supramarginal and the angular windings, both Fossae Sylvii were surrounded by atrophied windings. The upper part of the Gyr. centr. ant. of the right hemisphere was atrophied, the rest of the brain seemed unaffected. Sections showed that the left lateral ventricle



Fig. 1.

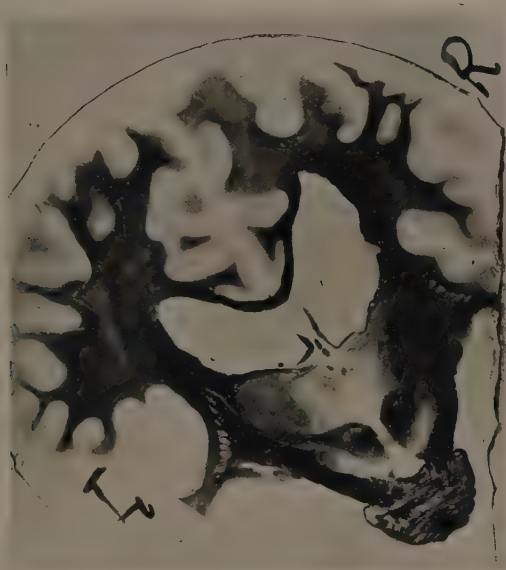


Fig. 2.

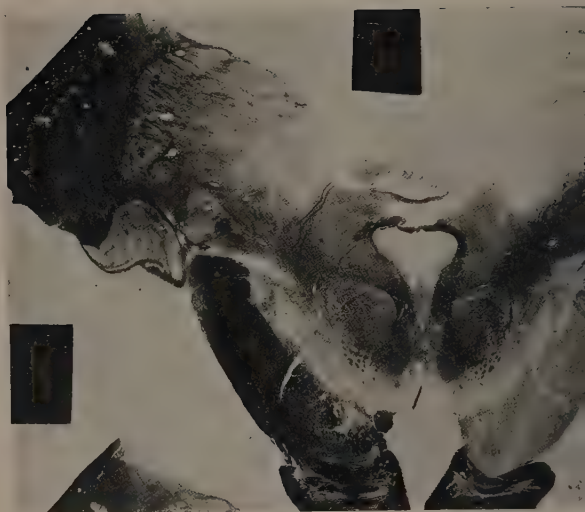


Fig. 7.

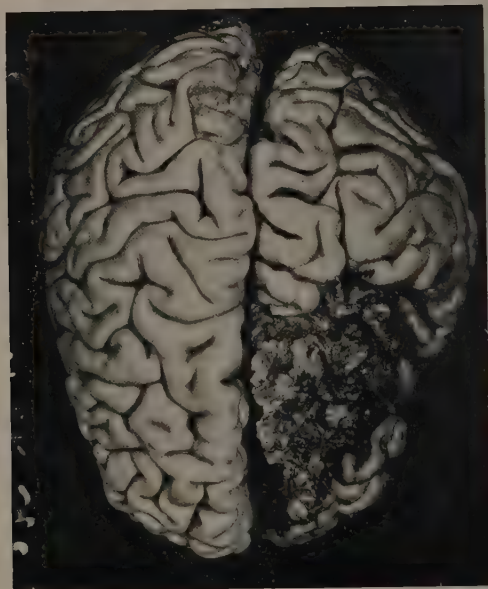


Fig. 8.



Fig. 9.

was much enlarged, especially in the neighbourhood of the paracentral gyrus, the wall of the ventricle was uneven, under the ependym many lacunae were found. The right lateral ventricle was somewhat enlarged, the wall was smooth. Both nucl. caudat. were much atrophied, macroscopic haemorrhages or softening were not present.

WEIGERT—PAL preparations showed a great loss of fibres in the atrophied winding, the marrow-fibres of the left praecentral winding were much reduced by the subependymal necrotic process. In the midbrain the inner part of the Pedunculus Cerebri was somewhat paler than the rest, a complete degeneration of the fronto-pontine tract could not be detected. Both pyramidal tracts were too pale in the Medulla Obl., as well as in the cord, while in the lower dorsal and in the lumbar segments these tracts were wholly degenerated. In this case both frontal lobes and both pyramidal tracts for the lower limbs were degenerated. In this case the result was a paraplegia in flexion.

Another patient, who also showed symptoms of paralysis in flexion, however in a somewhat different constellation, suffered from an organic dementia in the latter half of her 7th decennium. During life the nature of her disease was not clear, after death it proved to have been a case of general Palsy. She died at the age of 70 ; shortly before her death the following symptoms were noticed :

The patient is confused in mind, her speech is disjointed, she does not answer questions, but seems still to understand simple sentences. In her bed she lies on her back with both legs sharply flexed. The left arm is flexed into a right angle in the elbow, the right limbs can be moved actively, the left limbs are paralysed. The left lower limb is totally flexed in the knee, the right is bent into an acute angle Ph. I. The left leg can be moved passively in the knee, triflexion reflex immediately appearing when the foot is stimulated. Patellar and Achilles reflexes are unobtainable, BABINSKI's reflex is positive. The left arm is bent in the elbow, and lies motionless on the breast, the fingers at the ulnar side are bent in all joints and rigidly contracted. Passive movement is possible only to a limited extent in the elbow, the biceps and triceps jerks are obtainable, spontaneous movements do not occur in the arm. At the right extremities, no motor disturbances are to be observed, except the constant flexed condition of the leg with limited capacity of stretching ; the tendon reflexes are normal, the sole-reflexes are plantar, active movements are possible. The abdominal reflexes are obtainable on the right side, but not on the left.

After death it appeared that the cerebrum showed considerable atrophies: At the right hemisphere the entire frontal lobe was much atrophied as far as the Gyr. centr. ant., except the agranular zone of the upper winding, likewise the frontal Operculum and the base of the foremost central winding. All of the three temporal windings were much atrophied, the Gyr. central. post. was softened as far as the lower half, likewise the parietal and the occipital windings. The left hemisphere showed an atrophied frontal

lobe, just as the right, the anterior central winding, the frontal Operculum and the temporal windings were, however, in much better condition. The parietal and occipital windings showed no degenerations.

On the transverse sections an enormous Hydrocephalus was found, which extended upwards to a considerable degree into the central region, in this way undermining the fibres from the paracentral windings for the greater part. (Ph. 2). The Nucl. Lentiformes were somewhat atrophied on both sides, the Nucl. caudat. were very narrow.

The sections, which were stained according to the method of WEIGERT—PAL showed a marked difference between the left and right hemisphere. From the central and paracentral windings on the left side strong bundles of fibres extended to the Capsula Int. The bundles of the right side were very poor in fibres owing to a lack of fibres of the windings themselves, and the enormous enlargement of the lateral ventricle (Ph. 2). Similar sections stained with BÖHMER's haematoxyline showed excessive paralytical degenerations and a total destruction of the cyto-architectonics in the greatly atrophied windings; the slightly atrophied windings showed an inconsiderable degree of peri-vascular infiltration and vascular growth, the cyto-architectonics, however, were still clearly recognisable.

In the basal ganglia only extremely slight deviations were to be found, ganglion-cells were present in great numbers everywhere. The fibre-systems in the midbrain were not degenerated, the systems H1 and H2 of Forel, the Ansa Lenticularis, and the fibres about the Nucl. Ruber were entirely intact. In the Pons the right pyramidal tract was too pale, the transverse pons-fibres and also the pons-ganglia showed a normal aspect. The pyramidal tract from the right hemisphere was degenerated in the Med. Oblongata and the cord, and could be followed as such into the lumbal segments; in the lumbal segments it was found that the other pyramidal tract was not wholly intact; however, it contained a great many more fibres than the first-mentioned.

Therefore in the case of this woman the greater part of the right hemisphere had disappeared, in consequence of a paralytic process, while of the upper part of the anterior central winding, which was still preserved, the greater part of the descending fibres close under the cortex was interrupted by a subependymal necrosis. Of the other hemisphere only the base of the anterior central winding and the frontal lobe was affected, the lower parts of the brain showed no lesion that was worth mentioning.

In consequence of this the left extremities were both paralysed in flexion, while the right leg showed a pronounced tendency of flexion without actual paralysis. In this case there is already an indication of the analysis of the paraplegia in flexion in the tendency of flexion and the paralysis; in both legs the tendency of flexion has become manifest, only the leg, the pyramidal tract of which is degenerated has got paralysed in flexion.

With the patients now to be discussed, we shall be able to study more

closely the tendency of flexion, either combined with paralysis caused by attendant pyramidal disturbances or not, and localise it anatomically. This tendency of flexing the legs is invariably attended with incapacity to walk erect, that is to say, the movements required for walking can be executed, so that the patient, if supported, can walk a few paces, but very soon his knees begin to give way, or his legs slip away under him.

Symptoms of lesion of the pyramidal system occur only by way of exception, or are merely indicated, the "reflexes, dits de défense" are clear. In a very demonstrative way these symptoms are met with in the case of Mrs D.

In 1924 this patient began to complain of headaches, dizziness, and impaired eye-sight. On examination she was found to have a right-sided homonymous hemianopsia and optic neurotics. She was therefore trepanned occipitally on the left side, but no tumour tissue was found, though the cerebral pressure proved to be increased. In the course of years the condition grew worse and worse, the right arm became paralysed, while at the same time the deep sensibility in that arm practically disappeared. It was observed that the patient, who had, in the meantime become bedridden, was always lying in bed with her legs flexed in knees and hips, it appeared that she had lost the power to walk erect, in the same way as described above, although her legs were not paralysed. In connection with the hemianopsia the paralysis, and the sensibility disturbances in the right arm, it was now supposed that the tumour was to be found at the foot of the central windings, and tending downwards would destroy the Tract. Opt.

Shortly before death the general symptoms of increased intracranial pressure suddenly grew much more pronounced, the flexed condition of the legs at the same time gave way to a strongly marked stretched condition. More than 4 years after the beginning of the illness, death occurred under increasing coma.

On opening the cranium it was found that the windings of the cerebrum were flattened everywhere, the sulci were closed up, the right frontal lobe was about twice as thick as the left. Transverse sections brought to light a recent haemorrhage in a tumour in the front part of right frontal lobe, also in the left lobe tumour tissue was present. (Ph. 3). The right frontal lobe was considerably dilated owing to the haemorrhage and the tumour, so that the left lobe was compressed. On sections made farther back the tumour extended through both frontal lobes, terminating in the region of the Foramen Monroï. The base of the left central winding was compressed by the tumour, in the same way as the left For. Monroï, so that fibres radiating from that winding had greatly decreased in volume, and the left temporal and occipital ventricles were considerably dilated owing to the impeded passage of the ventricle-humour.

In the midbrain, the cerebellum and the Med. Obl. there were no deviations.

In the WEIGERT—PAL preparations the compressed central windings

of the left hemisphere proved to be poor in marrow-fibres, in the *Pedunculus Cerebri* the fibres on the left side going to the arm were degenerated.

In the case of this patient the symptoms pointing to lesion had been caused by pressure of the tumour on adjacent parts of the brain, the actual havoc made by the tumour was not diagnosed during life. The destruction of the frontal lobes caused a tendency of flexion of the legs, which did not culminate in a paraplegia in flexion, because there was neither paralysis nor lesion of the pyramidal tracts. The tendency of flexion disappeared towards the end, when through the considerable haemorrhage in the tumour of the right frontal lobe, the intracranial pressure increased so greatly, that the cerebrum ceased to function, causing the tendency of flexion to give way to decerebrate rigidity.

Another woman, who showed a constant flexed condition of the legs without paralysis, was the patient J.

Already at the age of 46 she began to suffer from a rapidly progressive organic dementia, so that in a short time she unlearned to perform her daily work, began to make mistakes in speaking and writing, and did not know her way about in the house any more. Epileptic or apoplectic attacks did not occur, neither did paralysis, only the left leg became a little shaky. An inquiry into the antecedents of the patient's parents brought to light, that the patient's mother had shown similar symptoms, which, however, did not appear before she was 74, death ensuing in a few months.

Two years after the beginning of the disease the patient was admitted into the hospital, she was much demented then, was quite incapable of speech, walked badly, and wanted assistance with everything. The very simplest actions, as e.g. conveying a piece of bread to her mouth were performed imperfectly, other actions serving a practical purpose were not noticed, she did not at all react on verbal orders given to her.

An examination, shortly before death gave the following results :

The patient lies in bed practically motionless, legs sharply flexed in hips and knees, and arms folded across breast. She can actively stretch her legs to the full extent, though the movements are slow. The patellar and Achilles jerks are not increased, neither knee nor foot-clonus are obtainable. the sole-reflexes are mostly plantar, sometimes uncertain on the right side, the *OPPENHEIM* reflex is dorsal on the right side. On stimulation of the foot or the lower part of the leg the trifleflexion reflex is immediately excited. In the arms the mechanical irritability of the muscles is very great. The reflexes are unchanged, the fingers of the left hand are contracted in a flexed position. The suction reflex is not clearly obtainable, although she seeks and follows with her lips an object held out to her. The "*RÜSSEL* reflex" is lively, the threat reflex is positive on both sides.

This patient died at the age of 53, in consequence of broncho-pneumonia. The disease was diagnosed as *PICK's Atrophy*, as the symptoms corresponded exactly to those mentioned in *GANS's* publication on this affection

and its differentiation from ALZHEIMER's disease. The total apraxis, the absence of hallucinations and delusions, the apathic nature of the disease, the absence of logoclonus, so typical for ALZHEIMER's disease, vacant facial expression, all these characteristic symptoms were uncommonly completely displayed by this woman.

On the cranium being opened this diagnosis was confirmed at first sight, as shown in Photo 4. An extreme atrophy of the frontal lobes, with a sharp demarcation on the line between BRODMAN's Regiones 6 and 4, could be ascertained immediately. Moreover region 32 on the medial side of the frontal lobe and the lowest temporal winding of the right hemisphere, the temporal pole, and the G. Submarg. were atrophied corresponding to regiones 20, 21, 38, and 40, likewise sharply demarcated from the surroundings. The atrophied windings were discoloured to a yellowish brown, and were somewhat firmer to the touch than the other windings.

When transverse sections were made, it was found that there was a considerable Hydrocephalus, especially in the frontal parts of the front cornua, the upper part of the Nucl. Caud. was greatly atrophied. Neither haemorrhages nor softenings were found, the vasa were not calcified, the cerebrum weighed 690 grams.

The histological examination showed a nearly total absence of ganglion-cells in the atrophied regions, senile plaques or ALZHEIMER's fibrillary degeneration were not present, further the typical degenerations as described by GANS were found.

WEIGERT—PAL preparations proved that the marrow fibres in the frontal windings had almost entirely disappeared, just as the frontopontine tracts in the Capsula Int. and in both Pedunculi Cerebri (Ph. 5). In the right Pedunculus Cerebri some medial bundles from the pyramidal tract were lacking. The fibre systems of the mid-brain, H1 and H2, the Ansa Lentic., the fibres about the Nucl. Ruber, the transverse Pons fibres were intact, only the hilus of the Nucl. Ruber was less clear than in normal cases. The Nucl. Ant. and Med. of the Thalamus seemed to be a little atrophied, the cells of the Subst. Nigra were pale and imperfectly formed.

This patient showed, even more than the preceding, a syndrome that had much in common with the classical cases of "Paraplegie en Flexion", dull facial expression, extreme organic dementia, uncleanliness, spasmodic fits of weeping and laughter, lack of spontaneous movements, flexed condition of the legs, unchanged tendon reflexes, increased flexion reflexes in the legs. The great difference is the absence of paralytic symptoms of the legs, although the power of walking erect had been lost. An anatomical examination revealed no pyramidal tract lesions, except some fascicles situated medially in the right Pedunculus Cerebri, which caused the paralysis of the left hand. The destruction of the frontal lobes had, therefore, given rise to predomination of the tendency of flexion of the lower limbs and the loss of the power to walk erect. A more complete,

perfect destruction of the frontal brain than took place in this woman suffering from PICK's Atrophy, can hardly be imagined.

The patients that have been discussed so far showed especially degeneration of the frontal brain, either combined with pyramidal tract lesion or not. In consequence of this a flexed condition of the legs had resulted, attend with paralysis, if the pyramidal tract system was degenerated. The lower portions of the brain were in all cases wholly or, for the greater part, intact. Another combination of lesions, unilateral degeneration of the frontal and central brain appears also to be able to cause symptoms of paraplegia in flexion as will be illustrated by the two cases now to be discussed.

The patient K. had to be admitted into the Ramaer Hospital, at the age of 63, because she had become paralysed on the left side in consequence of an attack of apoplexy.

In the hospital it was ascertained that the patient was quite paralysed atonically on the left side, arm and leg lacked all active motivity, tendon reflexes were unobtainable, with the exception of the triceps tendon reflex of the arm. The leg was kept flexed constantly in knee and hip, the BABINSKI and OPPENHEIM reflexes were negative. The left facialis was paralysed centrally, the ocular movements were possible in all directions, the pupils reacted on light.

After death, about 6 months after paralysis set in, it was found, when the cranium was opened, that the entire right hemisphere had softened, in the thickened pia mater hung a pulpy greyish yellow mass, in which it was still possible to recognise remains of the windings. (Ph. 6). The left hemisphere did not show degenerations externally, the wall of the vascular corona was thickened here and there. On making a section it was found that the whole right hemisphere, where it had not softened owing to softening of the marrow, was separated from the brainstem. Moreover the Nucl. Lenticularis, the lateral Nucl. Thalami, part of the Pedunculus Cerebri, and the greater part of the Pulvinar had disappeared.

No serious deviations were seen in the left hemisphere. Serial sections through the brainstem and the remains of the softened hemisphere stained in the usual ways, to study nerve fibres and cells, revealed the following results :

The Thalamus did not contain any recognisable ganglion-cells in a single nucleus, everywhere there was a considerable infiltration, at least, if larger and smaller foci had not dissolved the tissue. The Capsula Int. was not present, the Fasc. Lent. of FOREL did not contain fibres, the Fasc. Thalamo-Mammillaris was on the right side half as voluminous as on the left, but was well tintured, the Corp. Mamm. was on the right side half as big as on the left, in the most lateral part nerve cells were recognisable. The Fasc. H2 was poor in fibres on the right side, the Fasc. Retrofl. was the same on the right and left sides, the Nucl. Ruber was on the right

side a little flatter than on the left, the hilus was not perfectly formed, the Corp. Geniculata were lacking on the right side, the Pedunculus Cerebri did not contain fibres. (Ph. 7). The Subst. Nigra was not poor in cells on the right side, the cells, however, were all paler, and smaller and more irregular in form than on the left side, between the cells there was much pigment. In the Pons all fibres extending longitudinally were lacking on the right side, the Pons-ganglia and the transverse Pons fibres were the same on both sides. The region of the medial Pedunculus Lemnisci was fibreless on the right side, and could therefore be followed far into the Pons, in the interolivary region of the lemniscus fibreless regions were likewise to be seen. The pyramidal tract in the oblongata was entirely fibreless, just as the uncrossed tract. ant. and the crossed tract. lat. in the cord, the first-mentioned was to be seen as far as the lowest dorsal segments. In the basal ganglia of the sound hemisphere a number of lacunae occurred.

This patient differs indeed greatly from the ones that have just been described, although here also, just as with the others, the frontal and the central lobes, are quite destroyed, but the decay did not stop here, also the ganglion-cells were rendered quite incapable of function, as far as the Nucl. Ruber everything is decayed. This lesion consequently amounts to the decerebration, which ZELJONI, ROTHMANN, GOLZ and others performed on their animals, without observing a change in the tonus of the muscles of the extremities. With human beings such a decerebration apparently results in serious functional derangement. In the case of ordinary paralysis, owing to decay of the pyramidal tract, generally in the centre of the capsula int., the arm is indeed rendered powerless; the leg, however, in its excessively stretched condition can still be used for walking in the erect posture characteristic of man. In cases of paralysis in a flexed condition this difference between arm and leg is not extant, we might even say that in such cases it is just the other way round.

The leg in a flexed condition is eminently unfit to perform the movements required for walking, even without actual paralysis. Therefore it was impossible for the two first patients to walk. Consequently tendency of flexion of the legs must be looked upon as the expression of a regression of motility, the stretched leg being typical for the human species, just the same as the erect posture. As O. FÖRSTER remarks, theorising about the phylogenetic moment in the case of spastical paralysis, this tendency of flexing is still extant in the infant; paralysis occurring in the first months after birth results in a flexed condition, and not in a stretched condition, as is generally the case with adults. He is of opinion that subcortical influence is pre-eminently favourable for the flexed condition, and that the development of the pyramidal tract causes cortical influence to take the lead, and the stretched condition to pre-dominate. From the above clinical experiences I think I am justified in concluding, that this cortical influence should be ascribed to the frontal lobes; also with the infant the tendency of stretching gets the upper hand, not when the pyramidal tract is getting

fully developed, but much later, at the time of the myelinisation of the frontal lobes. Also phylogenetically this is more probable; not the pyramidal-tract system is the latest acquisition of the human species, this system being pretty fully developed with the higher mammals with their extremities flexed in walking; the strongly developed frontal lobes are much more specifically human, just as the erect posture with the tendency of extension of the legs.

The last patient shows us, where the tendency of flexion of the legs is located. With her, everything above the Nucl. Ruber had disappeared, causing a permanent flexed condition to become manifest. We know, however, from RADEMAKER's, R. MAGNUS's, and SHERRINGTON's experiments with animals, from clinical observations made by KINNIER WILSON and STENVERS, that decerebrate rigidity with extremities stretched to the utmost extent occurs in decerebration close under the Nucl. Ruber. Consequently in this nucleus or its immediate vicinity, the tendency of flexion is located, which during life is kept in check by the influence of the frontal lobes, to become manifest as soon as these lobes disappear. If there is at the same time a considerable degeneration of the pyramidal tract of the relative extremity, a paraplegia in flexion makes its appearance, otherwise the only consequence is a habitual flexed condition, and loss of the power of walking erect.

As a symptom of regression this syndrome is apt to occur with old persons, even if the whole frontal lobe has not disappeared, if, owing to many disseminated foci all possibilities of compensation are lost, this syndrome occurs, and is characterised by the lingering nature of the disease. Many patients mentioned in the literature on this subject show similar symptoms, although the entire frontal lobe proved not to be degenerated.

In contradistinction with this the brains of young persons can stand a considerable lesion of the frontal and central windings, which does not necessarily result in a paraplegia in flexion. SOUCQUES, for instance, described in the "*Revue Neurologique*" a 30 year old lueticus, with whom an entire hemisphere was practically decayed, in consequence of which an ordinary hemiplegia occurred, so that the man could use the stretched leg in walking. With old people paralysis in flexion can arise in a clearly localised way, as was the case with a patient, I could observe.

As early as 1918, at the age of 60, the patient E. was admitted into the hospital, because she had attempted suicide. During the 10 years she stayed there, she continually displayed the varying symptoms of a maniacal depressive psychosis, organic dementia was not diagnosed, neurological deviations were not found.

Her physical condition never gave rise to anxiety, till in November 1927, it was noticed that the patient walked with a certain amount of difficulty, caused by a little stiffness in the right leg.

A physical examination revealed the following facts:

Heart enlarged on the left side, at the apex systolic soufflé, pulse celer

and hard, abdominal reflexes all positive on the left side, on the right side positive in the upper region, for the rest negative. Patellar and Achilles jerks all increased, on the right side patellar clonus. Solereflexes dorsal on the right, on the left plantar. Standing and walking uncertain, spastic — paretical with the right leg.

In the early part of January of the next year the patient became very lethargic, she could not stand anymore, she proved to be suffering from a rightsided hemiplegia, with arm and leg in a sharply flexed position, also the right facialis was centrally paralysed.

Examination on the 3rd April '28.

The patient is always lying in bed turned on her left side, she is quite confused in mind, and continually of uncleanly habits, she can speak only a few monosyllables (yes and no). The right leg is sharply flexed, the right arm lies on the breast, flexed in the elbow, active movements are not possible in those extremities. The patellar and Achilles reflexes are lively on the right side, clonus is not obtainable, the trifleflexion reflex is very lively, the sole-reflex is dorsal.

On the right arm the ulnar fingers are contracted in a loosely flexed position, the arm can be a little stretched in the elbow, the right facialis is paralysed round the mouth.

The left leg and the left arm are not paralysed, the reflexes are normal, the left leg is often in a flexed position.

The facial expression is dull, occasionally interrupted by spasmodical fits of weeping and laughing, the eyes can be moved in all directions, the field of vision does not seem to be limited, speech is monotonous and restricted to a few words, simple questions are sometimes understood.

In May '28 the patients condition grew much worse, swallowing became difficult, broncho-pneumonia caused death in June.

The disease was diagnosed as a softening of the frontal and central windings of the left hemisphere. As this was a case of acute hemiplegia in flexion the expectation of finding a circumscribed defect of the parts mentioned was justified.

On the cranium being opened, it was found that this diagnosis was fully confirmed, as will be seen in photo 8, the frontal and central windings of the left hemisphere have indeed disappeared, only the orbital windings of the left hemisphere were still preserved, all the other frontal, and likewise the anterior and posterior central windings were quite softened. On dissecting the cerebrum also the marrow-cone of those windings proved to be softened, just as the marrow of the paracentral winding and the Insula. On the right hemisphere a slight softening proved to be present. The basal ganglia and the Caps. Int. were intact. The wall of the vascular corona showed slight protuberances in many places.

A histological examination of a winding that had remained intact, showed degenerations of the vascular walls, senile plaques were not found.

An examination of the brainstem by means of serial sections showed the following facts :

The medial and the anterior nuclei of the Thalamus have, for the greater part been destroyed by softenings on the left side. The Nucl. Lenticularis shows some lacunae, the Ansa Lentic., and FOREL's H2 are, however, well provided with fibres. The Caps. Int. does not contain any transverse fibres, only EDINGER's comb-system and a few fibre fascicles between the Nucl. Caud. and the putamen show marrow-sheaths. The temporal lobe is in a good condition.

In the Mesencephalon the left Pedunculus Cerebri contains marrow fibres only in the third lateral part, the Nucl. Ruber is well provided with fibres on both sides, still the hilus is better formed on the right side than on the left. (photo 9). The subst. nigra is the same on both sides. VICQ D' AZYR's Fasc. and FOREL's H1 are sufficiently tintured. In the Pons the fibres of the fronto-pontine and of the pyramidal tract are lacking, the fibres of the temporal-pontine tract terminated in the distal pontine nuclei. The Ganglia of the Pons and the transverse pontine fibres are not degenerated.

The Pyramidal tract from the left hemisphere was entirely degenerated in the Med. Oblongata and in the cord. The Pedunculus Lemnisci Med. was fibreless on the left side, in the interolivary part of the Lemnisci fibreless fascicles were also to be found.

This woman, therefore, suffered from paralysis in an acute form with the leg in a flexed position, owing to a circumscribed softening, while, although the cerebrum showed a few slight degenerations in the windings that had been spared, only one focus of any significance was to be found.

This case, of course, is a great deal different from the "Paraplegie en Flexion", which, indeed, seems to be the most usual form, in which paralysis of flexion of the legs occurs. The comparative frequency of this form can be accounted for by assuming, that the centra for maintaining an erect posture in walking are located in the frontal lobes of the cerebrum. These centra will, from the nature of things, have little or no influence on the arms, whereas for walking it is necessary that both legs co-operate to this end in the same degree, so that bi-lateral influence of the centra is essential. Consequently, if in a senile cerebrum there is something wrong with these centra, with slight degenerations in the pyramidal systems, this will be fatal, especially for the legs, and cause symptoms of paralysis with a tendency of flexion in the legs. Especially with the diffuse cerebral diseases of the senium, in which those portions of the brains which attained their full development latest, are often affected first and most seriously, and in which the tendency of regression is greatest, these symptoms will appear. The "Paraplegie en Flexion" should still be considered as the "Paraplegie des Vieillards", the name that the older French physicians gave to it.

Botany. — *Aggregation-substance in the terminal glands of Drosera.* By WILLEMINA M. COELINGH. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of September 28, 1929).

The process of aggregation in the tentacles of *Drosera* was seen for the first time by CH. DARWIN (1875) and was studied afterwards by A. F. W. SCHIMPER (1882), HUGO DE VRIES (1886), W. GARDINER (1886), Å. ÅKERMAN (1917) and others. It is generally described in the following way:

Strong protoplasmic currents occur in the tentacle cells. The single vacuole divides into several small ones, which incessantly change their forms and positions. Simultaneously the protoplasm increases in size at the expense of the cell sap. Aggregation always begins within the terminal gland and travels down the pedicel where it can be best observed. It decreases gradually from the top of the tentacle downwards.

Plants of *Drosera capensis* L., *D. binata* Labill. and *D. spatulata* Labill. were cultivated at a sunny place in a hothouse on peat, which stood in dishes of pottery containing about an inch of water. In another hothouse, which was cooler, *D. intermedia* Hayne, *D. rotundifolia* L. and *D. anglica* Huds. were cultivated in moist crushed peat. All grew very well and regularly produced flowers (except *D. binata*). During winter the three exotic specimens were exposed each night to a lamp of 1000 candle powers. Between the plants and the lamp a big glass trough with water was placed in order to avoid too high temperatures. The influence of the lamp was quite perceptible: the plants increased in size and flowered during winter. *D. capensis* was generally used for experiments.

I studied first of all the influence of the terminal gland on the distribution of the process of aggregation in the pedicel. To induce aggregation use was made of solutions of pepsine or of Liebig's meat extract.

If a tentacle from which the terminal gland has been removed, is cut from the leaf and placed into a solution of pepsine or meat extract, the distribution of the aggregation appears to be the same as in uninjured tentacles, the aggregation being always strongest in the part of the pedicel that was nearest to the gland. The "polarity", therefore, is not due to the fact that the cuticle of the gland is very much thinner than that of the pedicel and can be passed much easier by solutions.

The assumption was made that each gland regularly produces a substance which travels down the pedicels, not inducing aggregation itself, but bringing the cells into a state in which aggregation is possible

("aggregating substance"). The existence of such a substance has been vaguely suggested already by ÅKERMAN.

This hypothesis has been confirmed by the following experiments: Separated tentacles without terminal glands lose their power of aggregation in a solution of say pepsine, after having been immersed in water or a sugar solution for some days; the power of aggregation is maintained longest in the central part of the tentacle pieces. Nevertheless, one can make those tentacles aggregate again with an extract of the glands. This extract was made in the following way:

A great number of glands (from 15 to 30 leaves of *D. capensis*) were cut and placed in a few drops of water. After some days the colourless liquid was separated from the glands by filtration. Tentacle parts which did not aggregate any more with pepsine do aggregate if placed in this filtrate. In this case the cells at both ends of the pieces show the strongest aggregation, which proves that they have not been injured by the water or by the sugar solution.

TABLE I.
D. capensis.

| Solution | Number of parts | Aggregation |
|---|-----------------|-----------------------------|
| L's meat extract | 10 | 7 none, 3 weak |
| L's meat extract + extract of the glands | 8 | 2 strong, 5 obvious, 1 none |

Observation of the results after 20 hours.

The extract can be boiled or evaporated without losing its power. On the other hand it cannot be kept longer than a few days; the active substance seems destroyed, probably by the action of micro organisms. The dried extract can be kept infinitely.

The extract of *D. capensis* causes aggregation also in the cells of the five other specimens mentioned. The material of these specimens was not sufficient to make an extract from their glands without destroying the plants.

TABLE II.

| Solution | <i>D. rotundifolia</i> | <i>D. intermedia</i> | <i>D. spathulata</i> | <i>D. binata</i> | <i>D. anglica</i> |
|--|------------------------|----------------------|----------------------|------------------|-------------------|
| | Aggregation | | | | |
| Pepsine | none | none | none | none | none |
| Pepsine + extract of the glands of <i>D. capensis</i> | rather strong | rather weak | rather strong | obvious | obvious |

Observation of the results after 24 hours.

At first sight one might think the aggregating property of the extract due to substances exuded from wounded cells. But this cannot be the case. The extract of glands was compared with one that was made in the same way from pieces of leaf tissue without any tentacles. The first fluid caused aggregation, the latter had no effect at all in the same concentration.

TABLE III.
D. capensis.

| Solution | Aggregation |
|-----------------------------------|-----------------------|
| Pepsine 1 0/0 | Very weak to weak |
| Extract of the glands 1 0/0 | Weak to rather strong |
| Extract of the leaf pedicel 1 0/0 | Very weak to weak |

Observation after 13 hours.

It appeared that aggregation is possible also outside of the tentacle cells. So it was observed in the cells of the leaf, in the calyx, in the bracts and also in the hairs and papillae which cover the green parts of the plant.

It seems that the two kinds of papillae too have the power of producing the "aggregating substance", although not in the same degree as the tentacle glands.

The extract of the glands is not the only substance inducing aggregation in tentacle pieces which do not aggregate any more with pepsine or meat extract. I mention first of all saliva.

Saliva can be boiled a long time and filtered without losing its aggregating property.

TABLE IV.
D. capensis.

| Solution | Aggregation |
|---------------|---------------|
| Pepsine | None |
| Boiled saliva | Rather strong |

Observation after 13 hours.

The part of dried saliva which is soluble in alcohol 96 % causes aggregation as well as the rest.

KCNS has not any effect.

These three experiments show that the acting substance in saliva is neither a ferment, nor albumen, nor KCNS.

The salts which have been found in saliva are, K, Na, Ca and Mg salts of the acids H_2SO_4 , H_3PO_4 , HCl and H_2CO_3 .

Experiments with these salts showed that the phosphates are the only ones which have the power to induce aggregation.

I determined the weakest solution of KH_2PO_4 , causing some aggregation in tentacle pieces which did not aggregate any more with meat extract.

The limit appeared to be a concentration of about 0.01 %. The limit for the action of saliva was found at a dilution of about 2 parts of saliva to 7 parts of water. This dilution contains, owing to the concentrations given in the book of BETHE, about 0.02 % orthophosphates. The numbers given here have no absolute value, the salt concentration of saliva can vary a good deal. It, therefore, seems probable that the aggregating property of saliva is due to the phosphates it contains.

Strong aggregation was caused also by the following amino acids: asparagine, aspartic acid and alanine. Less by leucine and glycine.

Practically no results at all have been obtained with tyrosine, kreatine and urea.

TABLE V.
D. capensis.

| Solution | Aggregation |
|---------------------------------|-------------|
| Pepsine $\frac{1}{3}$ 0/0 | Weak |
| Asparagine, saturate | Very strong |
| Tyrosine, saturate | None |
| Aspartic acid $\frac{1}{2}$ 0/0 | Very strong |
| Urea | Very weak |

Observation after 17 hours.

Taka diastase and Rhenania trypsin showed a weak influence. No results have been obtained with some compounds which reduce the surface tension (saponine, amylalcohol) and some which increase the swelling of colloids (e.g. KCNS).

I must reject the possibility that the substances mentioned should act only because of their pH . The following evidence may be given as an example. Two fluids which each cause aggregation, one showing alkaline (saliva), the other acid reaction (a solution of KH_2PO_4), were mixed together, so that the mixture possessed the same pH as was shown by the solution of pepsine which was used for a control. It appeared that the mixture caused aggregation whereas the pepsine caused none.

TABLE VI.

D. capensis.

| Solution | P _H | Aggregation |
|---|----------------|---------------|
| Pepsine | 5.1 | None |
| KH ₂ PO ₄ 2 0/0 | 3.4 | Rather strong |
| Boiled saliva | — | Strong |
| Saliva + KH ₂ PO ₄ , 5 to 4 | 5.1 | Very strong |

Observation after 17 hours.

The substances and solutions mentioned which cause aggregation in cells which cannot aggregate any more with pepsine or meat extract are also able to make normal, uninjured tentacles aggregate. In this case, however, pepsine and meat extract have a much more powerful action and cause stronger aggregation. The concentration limit was found lower for pepsine than e.g. for asparagine if fresh, uninjured leaves were used.

A full account of my experiments will be given later.

LITERATURE.

Å. ÅKERMAN, 1917. Untersuchungen über die Aggregation in den Tentakeln von *Drosera rotundifolia*. Botaniska Notizer p. 145.

A. BETHE, G. v. BERGMANN, G. EMDEN, A. ELLINGER, 1927. Handbuch der norm. u. pathol. Physiologie IIIer Teil.

CH. DARWIN, 1875. Insectivorous Plants. Revised by FR. DARWIN 1888.

W. GARDINER, 1885. On the Phenomena accompanying Stimulation of the Gland-cells in the Tentacles of *Drosera dichotoma*. Proc. Royal Soc. of London 1886 Vol. 39, p. 229,
A. F. W. SCHIMPER, 1882. Notizen über insectenfressenden Pflanzen. Bot. Ztg. 40, p. 225.

H. DE VRIES, 1886. Ueber die Aggregation im Protoplasma von *Drosera rotundifolia*. Bot. Ztg. 44, p. 1.

Utrecht, September 1929.

Botanical Laboratory.

Mathematics. — *Zwei Kongruenzen von biquadratischen Raumkurven zweiter Art.* Von J. W. A. VAN KOL. (Communicated by Prof. HENDRIK DE VRIES.)

(Communicated at the meeting of September 28, 1929).

§ 1. Zuerst untersuchen wir die Kongruenz der biquadratischen Raumkurven zweiter Art k^4 , welche durch sechs gegebene Punkte A, A_1, \dots, A_5 gehen und eine durch A gehende Gerade t ausser A noch zweimal treffen. Wir gelangen zu einer Abbildung dieser Kongruenz auf einen Punktfeld, wenn wir als Bild einer Kurve k^4 den Punkt K betrachten, den sie ausser t mit einer durch t gelegten Ebene α gemein hat. Diese Abbildung ist offenbar eineindeutig. Durch einen beliebigen Punkt K von α geht eine Fläche zweiter Ordnung, welche überdies A_1, \dots, A_5 und t enthält und auf dieser Fläche gibt es eine Kurve k^4 , welche durch K geht und t dreimal trifft.

§ 2. A ist ein singulärer Punkt; in A bildet sich ab das System der ∞^1 Kurven k^4 , welche α in A berühren; dieses System liegt auf der Fläche zweiter Ordnung, welche A_1, \dots, A_5 und t enthält und α in A berührt.

Die kubische Raumkurve k^3 , welche durch A_1, \dots, A_5 geht und t zweimal trifft, hat mit α ausser t einen Punkt S gemein. Auch S ist ein singulärer Punkt; in S bildet sich ab das System der ∞^1 ausgearteten Kurven k^4 , welche bestehen aus k^3 und den Geraden, welche k^3 aus A projizieren.

§ 3. Ausser dem oben schon erwähnten System enthält unsere Kongruenz noch fünf Systeme von ∞^1 ausgearteten Kurven k^4 . Die Gerade AA_i ($i = 1, \dots, 5$) wird nämlich durch die kubischen Raumkurven, welche durch A_k, A_l, A_m und A_n gehen, t zweimal und AA_i einmal treffen und also auf der Fläche zweiter Ordnung liegen, welche durch A_k, A_l, A_m und A_n geht und die Geraden t und AA_i enthält, zu ∞^1 ausgearteten Kurven k^4 ergänzt. Dieses System wird abgebildet auf die Gerade, welche die eben genannte Fläche zweiter Ordnung mit α ausser t gemein hat.

§ 4. Es sei k_l die Bildkurve des Systems Σ_1 der ∞^1 Kurven k^4 , welche eine gegebene Gerade l treffen. Auf jeder Fläche zweiter Ordnung, welche A_1, \dots, A_5 und t enthält, gibt es zwei Kurven von Σ_1 , welche l treffen, und die Kurve k^3 wird durch die drei Geraden, welche durch A gehen und k^3 und l treffen, zu drei ausgearteten Kurven von Σ_1 ergänzt.

Hieraus folgt, dass k_1 eine Kurve fünfter Ordnung ist, welche in A einen Doppelpunkt und in S einen dreifachen Punkt hat.

Analog beweist man:

Das System der Kurven k^4 , welche eine Gerade durch A_i noch einmal treffen, wird abgebildet auf eine Kurve k_{ii} dritter Ordnung, welche in S einen Doppelpunkt hat und durch A geht.

Das System der Kurven k^4 , welche eine Gerade durch A noch einmal treffen, wird abgebildet auf eine durch A gehende Gerade g .

Das System der Kurven k^4 , welche durch einen zweiten gegebenen Punkt B von t gehen, wird abgebildet auf eine Kurve k_B dritter Ordnung, welche in S einen Doppelpunkt hat und durch A geht.

Eine Kurve k_1 trifft eine Kurve k_m , eine Kurve k_{mi} , eine Gerade g und eine Kurve k_B bzw. in 12, 7, 3 und 7 nicht singulären Punkten. Hieraus ergibt sich:

Es gibt zwölf Kurven k^4 , welche zwei gegebene Geraden treffen.

Es gibt sieben Kurven k^4 , welche eine gegebene Gerade treffen und durch einen zweiten gegebenen Punkt von t gehen.

Die Kurven k^4 , welche eine gegebene Gerade l treffen, bilden eine Fläche O_1 zwölfter Ordnung, welche in den Punkten A_i fünffache Punkte und in A einen neunfachen Punkt hat; t ist eine siebenfache und l eine einfache Gerade von O_1 . Weiter lässt es sich zeigen, dass die Geraden AA_i Doppelgeraden sind und dass k^3 eine dreifache Kurve ist.

Die Kurven k^4 , welche durch einen zweiten gegebenen Punkt B von t gehen, bilden eine Fläche siebenter Ordnung, welche in A_i dreifache Punkte und in A und B fünffache Punkte hat¹⁾.

§ 5. Es sei k_γ die Bildkurve des Systems Σ_2 der ∞^1 Kurven k^4 , welche eine gegebene Ebene φ berühren. Auf einer Fläche zweiter Ordnung, welche A_1, \dots, A_5 und t enthält, gibt es ∞^1 Kurven k^4 , welche auf dem Kegelschnitt, den diese Fläche mit φ gemein hat, eine biquadratische Involution bestimmen. Auf dieser Fläche gibt es also sechs Kurven von Σ_2 . Die Kurve k^3 wird durch die drei Geraden, welche durch A und die Treffpunkte von k^3 und φ gehen, zu drei ausgearteten Kurven von Σ_2 ergänzt, welche je doppelt zu rechnen sind. Aus dem Vorhergehenden folgt, dass k_γ eine Kurve zwölfter Ordnung ist mit sechsfachen Punkten in A und S .

Eine Kurve k_φ trifft eine Kurve k_1 , eine Kurve k_{ii} , eine Gerade g , eine Kurve k_B und eine Kurve k_ψ bzw. in 30, 18, 6, 18 und 72 nicht singulären Punkten. Hieraus ergibt sich:

Es gibt 30 Kurven k^4 , welche eine gegebene Gerade treffen und eine gegebene Ebene berühren.

Es gibt 18 Kurven k^4 , welche durch einen zweiten gegebenen Punkt von t gehen und eine gegebene Ebene berühren.

¹⁾ Dr. G. SCHAAKE hat diese Fläche untersucht. Siehe diese Proceedings, 32, S. 110.

Es gibt 72 Kurven k^4 , welche zwei gegebene Ebenen berühren.

Die Kurven k^4 , welche eine gegebene Ebene φ berühren, bilden eine Fläche O_7 30. Ordnung, welche in den Punkten A_i zwölffache Punkte und in A einen 24-fachen Punkt hat; t ist eine 18-fache Gerade, $A A_i$ sind sechsfache Geraden und k^3 ist eine sechsfache Kurve von O_7 . Weil eine durch l gelegte Ebene mit O_7 ausser l eine Kurve elfter Ordnung gemein hat und es zwei Kurven k^4 gibt, welche l zweimal treffen (siehe § 6), ist die Berührungskurve von O_7 mit φ von der Ordnung $11 - 2 \cdot 2 = 7$.

§ 6. Die oben untersuchte Kongruenz ist von der ersten Ordnung und von der zweiten Klasse. In § 1 hat es sich gezeigt, dass durch einen beliebigen Punkt K eine Kurve k^4 geht. Weiter gibt es zwei Kurven k^4 , welche eine beliebige Gerade l zweimal treffen. Denn die biquadratischen Raumkurven zweiter Art, welche durch A_1, \dots, A_5 gehen und l zweimal und t dreimal treffen, liegen auf der kubischen Regelfläche, welche durch A_1, \dots, A_5 geht und auf welcher l eine einfache und t eine Doppelgerade ist; durch einen Punkt A dieser Doppelgerade gehen offenbar zwei Kurven k^4 . Diese Eigenschaft können wir auch in folgender Weise beweisen. Die Kurven k^4 von Σ_1 entsprechen den Punkten von l eindeutig. Das System Σ_1 und auch die Bildkurve k_l ist also vom Geschlecht null. k_l hat somit ausser S und A noch $6 - 3 - 1 = 2$ Doppelpunkte; d.h. es gibt zwei Kurven von Σ_1 , welche l zweimal treffen.

§ 7. Betrachten wir die Fläche F_1 gebildet von den biquadratischen Raumkurven zweiter Art, welche durch fünf gegebene Punkte A_1, \dots, A_5 gehen, zwei gegebene Geraden a_1 und a_2 treffen und eine gegebene Trisekante t haben. Aus einer in § 4 abgeleiteten Anzahl folgt, dass t eine zwölffache Gerade von F_1 ist, während a_1 und a_2 Doppelgeraden sind. Es sei F^2 eine Fläche zweiter Ordnung, welche durch A_1, \dots, A_5 geht und t enthält. Der Durchschnitt von F^2 und F_1 besteht aus der zwölffachen Gerade t , aus den vier auf F^2 liegenden biquadratischen Raumkurven zweiter Art, welche durch A_1, \dots, A_5 gehen, a_1 und a_2 je einmal und t dreimal treffen und aus der auf F^2 liegenden kubischen Raumkurve, welche durch A_1, \dots, A_5 geht und t zweimal trifft. Diese kubische Raumkurve ist viermal zu rechnen, weil sie durch die vier Geraden, welche sie und die Geraden a_1, a_2 und t (ausser den Schnittpunkten von t und der genannten kubischen Raumkurve) zu vier biquadratischen Raumkurven von F_1 ergänzt wird. Der Durchschnitt von F^2 und F_1 ist also von der vierzigsten Ordnung. F_1 ist somit eine Fläche 20. Ordnung, welche achtfache Punkte in A_1, \dots, A_5 hat.

Analog beweist man:

Die biquadratischen Raumkurven zweiter Art, welche durch fünf gegebene Punkte A_1, \dots, A_5 gehen, eine gegebene Gerade a treffen, eine gegebene Trisekante t haben und eine gegebene Ebene φ berühren,

bilden eine Fläche F_2 48. Ordnung, welche 18-fache Punkte in A_1, \dots, A_5 hat. a ist eine sechsfache und t eine 30-fache Gerade von F_2 .

Weil eine durch a_1 gelegte Ebene mit F_1 auszer a_1 eine Kurve 18. Ordnung gemein hat und es drei biquadratische Raumkurven von F_1 gibt, welche a_1 zweimal treffen (siehe § 6), ist die Berührungskurve von F_2 mit der Ebene φ von der Ordnung $18 - 2 \cdot 3 = 12$.

§ 8. Wir untersuchen noch die Kongruenz der biquadratischen Raumkurven zweiter Art k^4 , welche durch vier gegebene Punkte A_1, \dots, A_4 gehen, eine gegebene Gerade a treffen, eine gegebene Doppelsekante b und eine gegebene Trisekante t haben. Wir gelangen in folgender Weise zu einer einzuwertigen Abbildung dieser Kongruenz auf einen Punktfeld α . In α nehmen wir zwei Punkte P und Q an. Die Strahlenbüschel (P, a) und (Q, a) seien projektiv bezogen auf die Punktreihen von a bzw. b . Es seien p, q_1 und q_2 die Strahlen von (P, a) bzw. (Q, a) , welche den Punkten A, B_1 und B_2 entsprechen, in denen eine Kurve k^4 a bzw. b trifft. Die Punkte $p q_1$ und $p q_2$ betrachten wir als Bilder von k^4 . In einen beliebigen Punkt von α bildet sich eine Kurve k^4 ab.

§ 9. Der singuläre Punkt P ist das Bild der ∞^1 Kurven k^4 , welche durch den dem Strahle PQ zugeordneten Punkt L von b gehen und eine Fläche λ^{12} zwölfter Ordnung bilden, welche fünffache Punkte in A_1, \dots, A_4 und L hat und auf welcher a eine einfache, b eine Doppel- und t eine siebenfache Gerade ist. Diese Eigenschaften von λ^{12} lassen sich in derselben Weise zeigen wie die in § 7 genannten Eigenschaften von F_1 .

Der singuläre Punkt Q ist das Bild der ∞^1 Kurven k^4 , welche durch den dem Strahle PQ zugeordneten Punkt K von a gehen und die kubische Regelfläche κ^3 bilden, welche durch A_1, \dots, A_4 und K geht und auf welcher b eine einfache und t eine Doppelgerade ist.

Die Gerade PQ ist die Bildgerade der singulären Kurve k^4 , welche durch K und L geht.

Es gibt vier kubische Raumkurven k_i^3 ($i = 1, \dots, 4$), welche durch A_1, \dots, A_4 gehen, und a und b je einmal und t zweimal treffen. k_i^3 wird durch die Geraden, welche b, t und k_i^3 treffen, zu ∞^1 ausgearteten Kurven k^4 ergänzt. Jede Kurve dieses Systems hat einen Bildpunkt im Schnittpunkt S_i der Strahlen von (P, a) und (Q, a) , welche den Punkten $a k^3$ und $b k_i^3$ entsprechen.

Die vier Punkte S_i sind singuläre Punkte. Die Kurven k^4 , welche sich in S_i abbilden, bestehen aus k_i^3 und den Erzeugenden der kubischen Regelfläche, von welcher b und t zwei Leitgeraden sind und k^3 eine Leitkurve ist.

Der Kegelschnitt k_i^2 , der durch A_k, A_l und A_m geht und b und t trifft, wird durch die Kegelschnitte, die durch A_i gehen, in der Ebene $A_i t$ liegen und a, b und k_i^2 (auszer dem Punkt $k_i^2 t$) treffen, zu ∞^1 aus-

gearteten Kurven k^4 ergänzt, welche sich abbilden in zwei singuläre Punkte S_{11} und S_{12} .

Es gibt noch acht singuläre Punkte S_{ik} ($i=1, \dots, 4$; $k=1, 2$). S_{11} und S_{12} sind die Bilder von ∞^1 Kurven k^4 , welche bestehen aus k_i^2 und einem in der Ebene $A_i t$ liegenden Kegelschnittebüschel.

§ 10. Auszer den oben schon erwähnten können wir noch die folgenden Systeme von ∞^1 ausgearteten Kurven k^4 angeben.

Die durch A_i gehende Transversale von a und t wird durch die kubischen Raumkurven, welche durch A_k , A_l und A_m gehen, die Transversale (auszer ihrer Treffpunkt mit t) treffen, b und t zweimal treffen und auf der Fläche zweiter Ordnung liegen, welche durch A_k , A_l und A_m geht und b und t enthält, zu ∞^1 ausgearteten Kurven k^4 ergänzt. Es gibt vier derartige Systeme, welche sich abbilden auf vier Strahlen von (P, a) .

Die durch A_i gehende Transversale von b und t wird durch die kubischen Raumkurven, welche durch A_k , A_l und A_m gehen, die Transversale und a und b einmal und t zweimal treffen, zu ∞^1 ausgearteten Kurven k^4 ergänzt. Die vier derartigen Systeme bilden sich ab auf vier Strahlen von (Q, a) und auf vier kubische Kurven, welche je durch Q , S_1, \dots, S_4 gehen und in P einen Doppelpunkt haben. Es lässt sich zeigen, dass die kubischen Raumkurven, welche durch A_k , A_l und A_m gehen, t zweimal treffen, und a , b und die durch A gehende Transversale von b und t einmal treffen, eine Fläche elfter Ordnung bilden, welche fünffache Punkte in A_k , A_l und A_m hat und auf welcher a eine einfache, b eine Doppel-, die genannte Transversale eine vierfache und t eine sechsfache Gerade ist.

Auf der Fläche zweiter Ordnung, welche durch A_k , A_l und A_m geht und b und t enthält, liegen zwei Systeme von ∞^1 kubischen Raumkurven, welche durch A_k , A_l und A_m gehen, a einmal und b und t zweimal treffen, und durch die Geraden, welche durch A_i gehen und diese Kurven und t in verschiedenen Punkten treffen, zu zwei Systemen von ∞^1 ausgearteten Kurven k^4 ergänzt werden und je auf einen Strahl von (P, a) abgebildet werden. Es gibt offenbar acht derartige Systeme.

Es gibt ∞^1 kubische Raumkurven, welche durch A_1, \dots, A_4 gehen, b einmal und t zweimal treffen und eine biquadratische Fläche bilden, welche Doppelpunkte in A_1, \dots, A_4 hat und auf welcher b eine einfache und t eine Doppelgerade ist. Jede derartige kubische Kurve wird durch drei Transversalen von a , b und t zu ausgearteten Kurven k^4 ergänzt. In dieser Weise erhalten wir ein System von ausgearteten Kurven k^4 , das abgebildet wird auf einen Kegelschnitt, der durch P und Q geht, und auf eine biquadratische Kurve, welche durch S_1, \dots, S_4 und Q geht und in P einen dreifachen Punkt hat; überdies geht der Kegelschnitt durch vier Punkte S_{ik} und die biquadratische Kurve durch die anderen vier.

§ 11. Es sei k_l die Bildkurve des Systems Σ_3 der ∞^1 Kurven k^4 ,

welche eine gegebene Gerade l treffen. Durch einen Punkt von a gehen drei und durch einen Punkt von b zwölf Kurven von Σ_3 (siehe § 9). k_1 ist also eine Kurve 18. Ordnung, welche in P einen zwölffachen und in Q einen sechsfachen Punkt hat. Weiter hat k_1 einfache Punkte in S_{ik} und dreifache Punkte in S_i .

Das System der ∞^1 Kurven k^4 , welche eine Gerade l durch A_1 noch einmal treffen, wird abgebildet auf eine Kurve k'_1 elfter Ordnung, welche einen siebenfachen Punkt in P , einen vierfachen Punkt in Q , einfache Punkte in S_{ik} ($i \neq 1$) und Doppelpunkte in S_i hat.

Das System der ∞^1 Kurven k^4 , welche durch einen gegebenen Punkt T von t gehen, wird abgebildet auf eine Kurve k_T elfter Ordnung, welche einen siebenfachen Punkt in P , einen vierfachen Punkt in Q , einfache Punkte in S_{ik} und Doppelpunkte in S_i hat.

Eine Kurve k_1 schneidet eine Kurve k_m , eine Kurve k'_m und eine Kurve k_T bzw. in 100, 60 und 58 nicht singulären Punkten.

Hieraus ergibt sich:

Es gibt 50 Kurven k^4 , welche zwei gegebene Geraden l und m treffen.

Die Kurven k^4 , welche eine gegebene Gerade l treffen, bilden eine Fläche F_l 50. Ordnung, welche 20-fache Punkte in A_1, \dots, A_4 hat und auf welcher t eine 29-fache Gerade ist. Weiter lässt es sich zeigen, dass a und l dreifache Geraden sind und dass b eine zwölffache Gerade von F_l ist.

§ 12. Es sei Σ_4 das System der ∞^1 Kurven k^4 , welche a zweimal treffen. Jede Kurve von Σ_4 hat vier Bilder. Durch einen Punkt von a oder b gehen zwei Kurven von Σ_4 . Die Bildkurve k_a von Σ_4 ist also von der achten Ordnung und hat vierfache Punkte in P und Q . k_a hat Doppelpunkte in S_i , aber geht nicht durch S_{ik} .

Die Kurve k_a trifft eine Kurve k , eine Kurve k'_1 und eine Kurve k_T bzw. in 48, 28 und 28 nicht singulären Punkten. Hieraus folgt:

Es gibt 12 Kurven k^4 , welche a zweimal und eine gegebene Gerade l einmal treffen.

Die Kurven k^4 , welche a zweimal treffen, bilden eine Fläche F_a 12. Ordnung, welche fünffache Punkte in $A_1 \dots A_4$ hat und auf welcher t eine siebenfache Gerade ist und a und b Doppelgeraden sind.

§ 13. Untersuchen wir noch die Abbildung des Systems Σ_5 der Kurven k^4 , welche eine gegebene Ebene φ berühren. Durch einen Punkt von b gehen dreissig Kurven von Σ_5 (siehe § 7). Die ∞^1 Kurven k^4 , welche die kubische Regelfläche κ^3 bilden, schneiden auf der nodalen kubischen Kurve, welche κ^3 mit φ gemein hat, eine biquadratische Involution ein. Es gibt also auf κ^3 sechs Kurven von Σ_5 . Die Bildkurve k_p von Σ_5 ist somit von der Ordnung 42 und hat einen 30-fachen Punkt in P und einen 12-fachen Punkt in Q . Weiter hat k_p Doppelpunkte in S_{ik} und sechsfache Punkte in S_i .

Eine Kurve k_γ trifft eine Kurve k_l , eine Kurve k'_l , eine Kurve k_T , die Kurve k_a und eine Kurve k_ψ bzw. in 236, 144, 140, 120 und 544 nicht singulären Punkten. Hieraus ergibt sich:

Es gibt 118 Kurven k^4 , welche eine gegebene Gerade l treffen und eine gegebene Ebene φ berühren.

Die Kurven k^4 , welche eine gegebene Ebene φ berühren, bilden eine Fläche F_γ 118. Ordnung, welche 46-fache Punkte in A_1, \dots, A_4 hat und auf welcher t eine 70-fache Gerade ist. Weiter ist a eine sechsfache und b eine dreiszigfache Gerade auf F_γ . Weil eine durch l gelegte Ebene mit F_l ausser l eine Kurve 47. Ordnung gemein hat und es zwölf Kurven k^4 gibt, welche l zweimal treffen, ist die Berührungskurve von F_γ mit φ von der Ordnung $47 - 2 \cdot 12 = 23$.

Es gibt 30 Kurven k^4 , welche a zweimal treffen und eine gegebene Ebene φ berühren.

Es gibt 272 Kurven k^4 , welche zwei gegebene Ebenen φ und ψ berühren.

§ 14. Wir bemerken noch dasz die oben untersuchte Kongruenz von der dritten Ordnung und von der zwölften Klasse ist. Dies geht hervor aus oben abgeleiteten Eigenschaften.

Histology. — *Reversible changes in the epithelium of the tadpole. A test for differences in permeability caused by energy of radiation.*
By M. A. VAN HERWERDEN. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of September 28, 1929).

Some years ago I published a paper on reversible alteration in the epithelium of the living tadpole after treatment with diluted acetic acid ¹⁾. By this treatment the formerly invisible nuclei of the epithelium cells become discernable as soon as the acid penetrates the cell. The structure of the nucleus appears with all details and only disappears by returning the tadpole to the water. However, a too long exposure to the acetic acid solution (0.04—0.05 percent) changes this reversible state of the nucleus in an irreversible coagulation ²⁾. It takes some time, before the acid penetrates through the peripheral layer of the protoplasma and renders the nuclei visible. As one understands, this time-factor depends on other factors, the temperature being of considerable influence. If one takes tadpoles from the same parents and the same age, having been reared in the same aquarium, the permeability to acetic acid is about equal for the same temperature. Therefore, keeping the control-larvae under the same circumstances, it will be possible to use the appearance of the nucleus as a criterium for permeability to acetic acid.

In former experiments, described elsewhere ³⁾, I used this phenomenon to test the influence of radium rays on permeability, to demonstrate along this line of research, the distinct increase in permeability of the protoplasma by radium radiation. G. HANNEVART ⁴⁾ afterwards used this method to show the influence of different serum-injections on the permeability of the epithelium in the tadpole.

In the latter years I studied the permeability of the epithelium after radiation with different parts of the spectrum. As well as radium rays, the ultraviolet rays of the mercury quartz-lamp are able to promote the permeability of the protoplasma for acetic acid. In both cases the increase in permeability lasts a long time after the radiation has been applied. In most experiments a mercury quartz lamp on full power has been used, distance 0.6 m., $2\frac{1}{2}$ ampère, 220 volt, non alternative current. The tadpoles placed in a small glasscylinder with water, have been radiated from above. Only in two experiments, using a U. V. filter of LEHMANN, the tadpoles

¹⁾ These Proceedings, 27, 867, 1924.

²⁾ Protoplasma 1, 366, 1927.

³⁾ Archiv f. exp. Zellf. 1, 145, 1925.

⁴⁾ C.R. des séances d. l. soc. de Biol. 96, 423, 1927.

in a quartz holder with water have been radiated from the side. Distance 1 m., $2\frac{1}{2}$ ampère, 220 volt, non alternative current.

Radiation during 3—5 minutes with the mercury lamp without filter, is sufficient to obtain a considerable increase of permeability with a long lasting *after-effect*. Whereas the acetic acid needs at least 20 minutes in the control-larvae before it penetrates the epithelium cells, the nuclei of the tadpoles radiated during 3—5 minutes, get visible within 5 minutes after the animals have been put in the same 0.05 percent acetic acid solution.

This increase in permeability continues as an *after-effect* of radiation untill the tadpoles dy. Within 24 hours death is inevitable. The control-larvae however live on in good health. Sometimes one notes, before death, a light swelling of the tail and microscopically an extension of the alveoles of the formerly described subepithelial layer of the tadpole¹⁾. As soon as disturbance in the blood circulation begins, the tadpoles no longer are used for the experiments recording permeability.

In order to investigate by which rays this *after-effect* on permeability is obtained, different light filters have been applied. The putting of a mirror-glassplate (0.8 cm. diameter) between the mercurylamp and the cylinderglass with tadpoles, is sufficient to prevent afterwards the increase of permeability for acetic acid. The same may be obtained by using a filter of tartrazine solution. During these latter experiments a quartz glass filled with 0.05 percent tartrazine covered the cylinderglass with tadpoles, to which no other light rays were admitted than those permeating the tartrazine solution. A 0.05 percent solution of tartrazine in water (in a layer of 2 cm. height) absorbs after KÖNIG²⁾ rays below $480\text{ }\mu\mu$. From this appears that in these experiments the after-effect of the radiating energy on permeability is limited to the part of the spectrum which is absorbed by the tartrazine filter — that is to say to the ultraviolet rays.

A limited part within the ultraviolet area of the spectrum may be obtained by using the Woodsfilter by which principally rays between 340 and $330\text{ }\mu\mu$ are transmited³⁾. This filter made of cobaltglass with a film of nitroso-dimethyl-aniline, causes however a considerable reduction of the intensity of radiation⁴⁾. Notwithstanding this, one observes a distinct after-effect, as to the increase of permeability. Half an hour radiation and longer may be endured, without danger for life, when screening with this filter. The tadpoles remain in good health during many weeks. In contrast with the

1) Zeitschr. f. Zellf. und mikr. Anat. 7, 495, 1928.

2) Photogr. Bibliothek 25, Berlin 1909.

3) Photoelectr. Messmethoden. Handb. d. biol. Arbeitsmethoden Abderhalden Abth. 2, Teil 1, Lf. 40.

4) One easily might test this by radiating a photographic paper (f. i. daylight blue star paper) partly with, partly without a Woodsfilter. Radiation with ultraviolet rays during 40 minutes, screening with the Woodsfilter, causes less chemical decomposition than radition during 2 minutes without using this filter.

experiments without filter, one is enabled to study permeability in these larvae not only from hour to hour, but also from day to day. In some of the experiments permeability was still distinctly increased 24 hours after radiation. A longer after-effect may still be obtained by using the U. V. filter of LEHMANN (solution of nitrosodimethyl-aniline in water), or a solution of the same substance in glycerine, placed in a quartz holder immediately above the radiated tadpoles. By the U. V. filter rays between 400 and 300 $\mu\mu$ are transmitted. The glycerin solution is said to allow rays between 340 and 200 $\mu\mu$ to pass. In both cases the after-effect has been very clear, sometimes even after several days. Though radiation with ultraviolet rays, passing through these filters, may sometimes prove to be lethal to the larvae, many weeks passed, before death occurred. It is a remarkable fact, that tadpoles used for the acetic acid experiments, without exception, remained in better health and lived longer than those, which never had been treated with this acid solution, I don't know which is the reason of this greater resistance. Possibly, even probably, the P_H of the tissues have some influence on the admittance of the radiating energy. But one hardly can imagine that the short treatment with 0.05 percent acetic acid (hardly during 20 minutes, followed by transmittance in water) would have a lasting effect on the P_H concentration. One of the radiated larvae manifested a distinct degeneration of the tail nerves. There is absolutely no reason to consider this as a specific consequence of the ultraviolet rays. The deleterious effect manifests itself in different ways. A beginning metamorphosis is not stopped by intensive radiation (60 minutes radiation with the light of the mercury quartzlamp, filtered by nitrosodimethyl-aniline solution). The complete metamorphosis was accomplished 4 days after radiation had been applied; a fortnight afterwards the little frog still being alive.

The method of testing permeability by the appearance of the nuclei, also may be used for studying differences in permeability in daylight and darkness, if only one takes care to keep an equal temperature. In these experiments both groups of tadpoles have been put in two cylinder glasses with the same quantity of 0.05 percent acetic acid, one next to the other — one of the bowls being totally covered and surrounded by a black cylinder. While in diffuse daylight nuclei appeared after \pm 20 minutes, in the darkness often 70 minutes passed by, before the peripheral layer of the protoplasm had been trespassed by the acid. The difference is still greater, when in the meantime some of the larvae are radiated with a 200 Watt argalamp (heat rays being excluded by a solution of cuppersulfate). In the last case permeability is considerable increased.

With these radiation experiments beyond the ultraviolet part of the spectrum and with the experiments in the dark, any *after-effect* on permeability can't be traced. The tadpoles therefore had to be immersed from the beginning of the experiment in acetic acid solution instead of water, till the moment the nuclei appeared. Daylight and darkness experiments

in a room with closed window (mirrorglass 0.75 cm. diameter), reveal great differences in permeability. This proves that not exclusively the ultraviolet rays of the spectrum are responsible for the increase of permeability. In sunlight with closed windows, screening with a tartrazine filter (0.05 percent solution in a very thin glasscylinder of 2 cm. height), gives rise to an increase in permeability, when compared with the experiments in the dark at equal temperature. Still this filter absorbs rays below $480 \mu\mu$. So the effect has to be attributed to rays above $480 \mu\mu$.

Several investigators have been interested in the action of light and darkness on protoplasma permeability. For the plantcell I memorate the researches of STILES ¹⁾, MOLDENHAUER BROOKS ²⁾, HOAGLAND ³⁾ a.s.o. As to the plantcells, the possibility of analysing the salt concentration or the change of colour in the vacuole often enables to give a reliable criterium for judging permeability of the cell for different substances. In case of animals one has especially to rely on colour reactions. PACKARD ⁴⁾ f.i. used the alteration in colour of neutral red by ammonia, when studying the influence of different rays of the spectrum on permeability of protozoa. PACKARD also found, that it are not exclusively the ultraviolet rays, which further permeability. As a classical radiation experiment on living cells the "Strahlenstichmethode" of TCHAHOTINE ⁵⁾ has to be memorated. This author succeeded in obtaining a local increase of permeability in living egg cells under the influence of ultraviolet light ($280 \mu\mu$).

The method of revealing reversibly the structure of the nucleus in the living animal, makes possible the studying of alterations in permeability for acetic acid under different circumstances.

In the literature regarding this subject, I do not find publications on increased permeability, as an *after-effect* of radiation on protoplasma by the influence of radium and of ultraviolet light. I refer especially to the long lasting after-effect, which I observed even some days after radiation had been applied.

An increase of permeability after radiation with Röntgen rays has been described by several authors. Only isolated cases are known, where on the contrary a diminution of permeability seemed to occur. Possibly these contradictory results have to be attributed to the different phases of the colloid state of protoplasma during the exposure to Röntgen rays. In this connection I like to mention the interesting investigations of M. ZUELZER and E. PHILIPP ⁶⁾. These authors noticed a considerable influence of the momental viscosity of protoplasma on the permeability for Röntgen rays. E. SCHNEIDER ¹⁾ finds that Paramaecium is only susceptible to Röntgen

¹⁾ The new Phytologist **20**, 45, 1921.

²⁾ Protoplasma **1**, 305, 1927.

³⁾ Journal gen. Physiol. **10**, 121, 1927.

⁴⁾ Biol. Bull. **46**, 165, 1924; Journ. gen. Physiol. **7**, 363, 1925.

⁵⁾ C. R. d. I. Soc. de Biol. **84**, 164, 1921.

⁶⁾ Strahlentherapie **20**, 737, 1925.

rays at the alkaline side of the iso-electrical point, the penetration of Röntgen rays in the living organism depending therefore from the momental P_H of protoplasma.

For my own experiments there is no reason to make a finer regulation of the acetic acid solution, because excreta and secreta of the tadpoles are able, during the experiment, to make minute alterations in the acidity of the medium. This fact also explains, that very small alterations in the concentration of the acetic acid, do not necessarily influence the moment of appearance of the nuclei. With our present physical-chemical methods and physical-chemical lines of thought in biology, we should in general be careful not to loose sight of the lability of the living object on which the experiment is made.

The descriptions of my experiments will be published in the journal "Protoplasma". There will also be mentioned some views about the after-effect on the permeability of protoplasma, in relation to the influence of radiation on proteins. The after-effect on proteins has already been demonstrated in 1918 by W. T. BOVIE²⁾: Albumine radiated with ultraviolet rays at 0 degrees, only coagulated if brought in room temperature; remaining at 0 degrees no coagulation took place and could thus be deferred during a term desired.

Considering the *after-effect* of ultraviolet rays on protoplasma, one is inclined to believe that the displacement of electrons in the peripheral layer of protoplasma is lasting longer than under the simple light-dark experiment. In the latter case probably a very temporary displacement occurs in the electric double layer. As soon as radiation has stopped, the displacement is immediately restored. The increase in permeability can in this case only be tested by radiating the tadpoles directly in an acetic acid medium. The same happens, when the effect of the mercury lamp has been altered by screening with light filters, which absorb the ultraviolet rays.

The photo-electrical effect, viz. the emission of negative electrons under the influence of ultraviolet light on colloids, has been clearly demonstrated by ZWAARDEMAKER and HOGEWIND³⁾. This also accounts probably for the occurrence of differences of potential in bioelectrical phenomena of protoplasma. If these displacements of electrons are not immediately followed up by a state of equilibrium, they might alter for a certain time the permeability of protoplasma or they might lead to death. In this direction the problem of altered permeability by radiation has to be experimentally tested in the future.

¹⁾ Strahlentherapie 22, 92, 1926.

²⁾ Journ. f. med. Research 39, 271, 1918.

³⁾ These Proceedings, 21, 1146, 1919.

Mechanics. — Ueber eine Stabilitätsfrage beim gelenkig gelagerten, schwach gekrümmten Stabe. Von C. B. BIEZENO. (Communicated by Prof. W. VAN DER WOUDE).

(Communicated at the meeting of September 28, 1929).

1. Wir betrachten einen in seinen Endpunkten gelenkig gelagerten, schwach gekrümmten Stab, (Sehnenlänge $2l$) welcher in seiner Mitte mit einer Kraft $2P$ belastet ist (siehe Figur 1) und werfen die Frage auf,

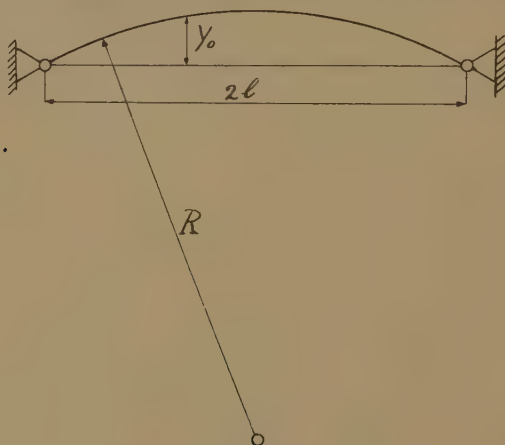


Fig. 1.

ob — und wenn ja, unter welchen Umständen — dieser Stab „durchschlagen“ kann.

Die Gleichung der elastischen Mittellinie im unbelasteten Zustande sei:

$$y_0 = \frac{1}{2R}(l^2 - x^2), \quad \dots \dots \dots (1)$$

wobei der Ursprung des Koordinatensystems in der Mitte der Verbindungslinie der Endpunkte angenommen worden ist; die Krümmung des Stabes sei so gering, dass der Krümmungsradius überall gleich R gesetzt werden kann.

Deutet man mit ϱ den Krümmungsradius im belasteten Zustand an, so gilt bekanntlich die Gleichung:

$$\frac{1}{\varrho} - \frac{1}{R} = \frac{M}{EI},$$

welche mit $M = -P(l-x) + Qy$ (siehe Fig. 2), unter den gebräuch-

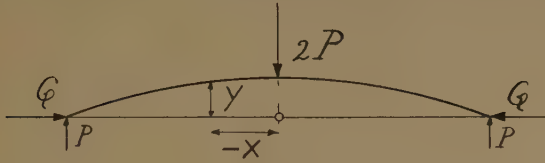


Fig. 2.

lichen Vernachlässigungen übergeht in:

$$-y'' - \frac{1}{R} = -\frac{P(l-x)}{EI} + \frac{Qy}{EI},$$

oder, mit $\frac{Q}{EI} = a^2$, in:

$$y'' + a^2 y = \frac{P(l-x)}{EI} - \frac{1}{R}.$$

Beschränken wir uns vorläufig auf den symmetrischen Fall, so gelten für die Lösung:

$$y = C_1 \cos ax + C_2 \sin ax + \frac{P}{Q}(l-x) - \frac{EI}{QR} \quad . \quad . \quad . \quad (2)$$

die Randbedingungen:

$$\begin{aligned} y' &= 0 \quad \text{für} \quad x=0 \\ y &= 0 \quad \text{,,} \quad x=l. \end{aligned}$$

Es wird somit:

$$C_1 = \frac{1}{a^2 R \cos al} - \frac{P}{a^3 EI} \operatorname{tg} al \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$C_2 = \frac{P}{a Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Nennt man die halbe Bogenlänge im unbelasteten Zustand L_0 , im belasteten Zustand L , und setzt man näherungsweise die im Querschnitt auftretende Normalkraft $= Q$, so gilt überdies:

$$L_0 - L = \frac{Ql}{EF} = \frac{a^2 Il}{F} = a^2 l^2 l \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(i = Tragheitsradius des Querschnittes).

Nun ist:

$$L_0 = \int_0^l \sqrt{1 + y_0'^2} dx = l + \int_0^l \frac{1}{2} y_0'^2 dx$$

$$L = \int_0^l \sqrt{1 + y'^2} dx = l + \int_0^l \frac{1}{2} y'^2 dx$$

sodass Gl. (5) übergeht in:

$$\int_0^l y_0^2 dx - \int_0^l y'^2 dx = a_1^2 l.$$

Unter Benutzung der Gleichungen 1...4 erhält man dann unter Einführung der Abkürzungen $\frac{R}{l} = p$, $\frac{i}{l} = q$, $\frac{P l^2}{EI} = P_1$, als Bedingungs-
gleichung für Q :

$$\begin{aligned} al \left\{ \frac{1}{p(al)^2} - \frac{P_1}{(al)^3} \sin al \right\}^2 & \left\{ -\frac{1}{4} \sin 2al + \frac{1}{2} al \right\} + \frac{P_1^2}{(al)^5} \left(\frac{1}{4} \sin 2al + \frac{1}{2} al \right) \cos^2 al + \\ & + \frac{P_1^2}{(al)^4} \cos^2 al + 2 \frac{P_1}{(al)^2} \left\{ \frac{1}{p(al)^2} - \frac{P_1}{(al)^3} \sin al \right\} (1 - \cos al) \cos al - \\ & - 2 \frac{P_1^2}{(al)^5} \sin al \cos^2 al - \frac{P_1}{(al)^2} \left\{ \frac{1}{p(al)^2} - \frac{P_1}{(al)^3} \sin al \right\} \cos al \sin^2 al = \\ & = \frac{1}{3 p^2} \cos^2 al - 2 (al)^2 q^2 \cos^2 al, \end{aligned}$$

welche reduziert werden kann zu:

$$\begin{aligned} (p P_1)^2 \left\{ 1 + \frac{\cos 2al}{2} - \frac{3}{4} \frac{\sin 2al}{al} \right\} - 2(p P_1) \left\{ \frac{1}{2} - \cos al + \frac{1}{2} al \sin al + \frac{1}{2} \cos 2al + \right. \\ \left. + \left\{ \left(\frac{al}{2} \right)^2 - \frac{(al)^4}{6} [1 - 6 p^2 q^2 (al)^2] (1 + \cos 2al) - \frac{al \sin 2al}{4} \right\} \right\} = 0. \end{aligned} \quad (6)$$

2. Die Gleichung (6) benutzen wir zum Entwerfen eines Diagrammes, welches für verschiedene Werte des Parameters pq den Zusammenhang zwischen den Grössen $p P_1 = \frac{R l}{EI} P$ und $Q_1 = a^2 l^2 = \frac{l^2}{EI} Q$ liefert. Am besten löst man — bei angenommenen (pq) -Werte u — die Gleichung (6) für verschiedene Werte von al als quadratische Gleichung in $p P_1$ auf.

Es entsteht dann im allgemeinen eine Schleifenkurve, wie Fig. 3 sie für die Werte $pq = \sqrt{\frac{1}{12\pi^2}}$, $\sqrt{\frac{1}{6\pi^2}}$, $\sqrt{\frac{1}{3\pi^2}}$, $\sqrt{\frac{3,45}{6\pi^2}}$, $\sqrt{\frac{2}{3\pi^2}}$ zeigt. Aus einer solchen Kurve ist unmittelbar die Kraft zu entnehmen, bei welcher der Stab „durchschlägt“. Tritt doch dieser Fall in dem Augenblicke ein, in dem zur Vergrößerung der Stabdurchbiegung keine Vergrößerung der Kraft P erforderlich ist, indem also im $(p P_1, Q_1)$ -Diagramm P ein Maximum erreicht.

Der Wert dieses Maximums, welcher natürlich aus Gl. 6 zu berechnen wäre, kann mit genügender Genauigkeit der Fig. 3 entnommen werden.

Trägt man in einem neuen Diagramm zu jedem (pq) -Wert als Abszisse den zugehörigen maximalen (pP_1) -Wert als Ordinate auf (vergl. Fig. 4), so kann für jeden vorliegenden Fall die „zum Durchschlagen“ erforderliche Kraft unmittelbar berechnet werden.

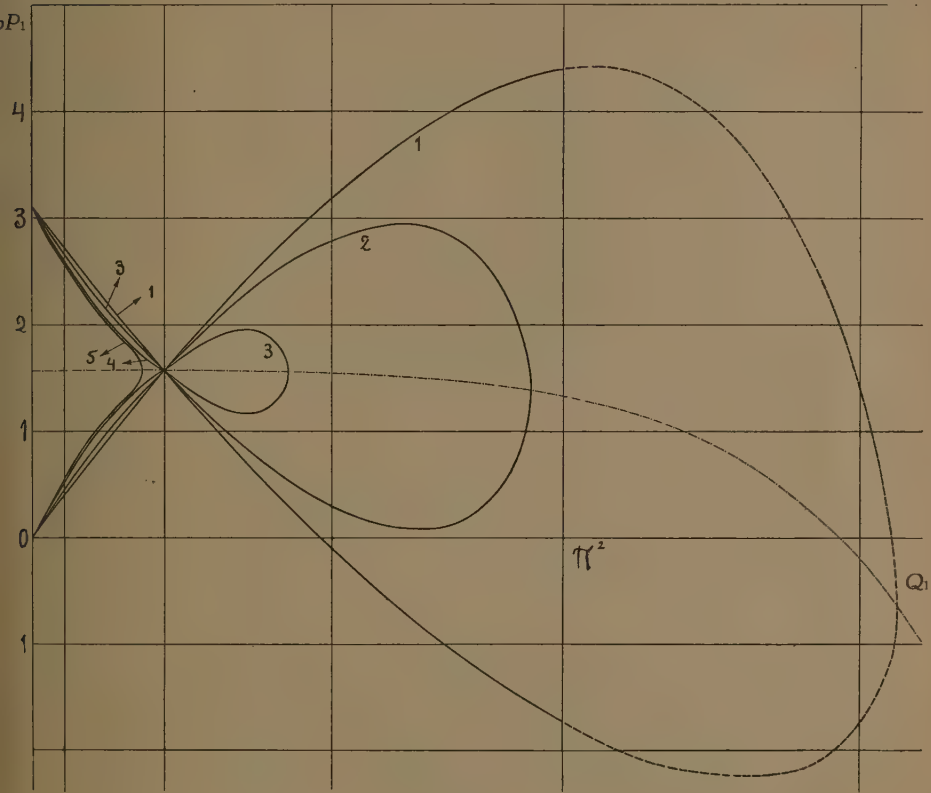


Fig. 3.

Die Zahlen 1, 2, 3, 4, 5 bezeichnen bzw. die (pP_1, Q_1) -Kurven welche zu den Werten

$$pq = \sqrt{\frac{1}{12\pi^2}}, \sqrt{\frac{1}{6\pi^2}}, \sqrt{\frac{1}{3\pi^2}}, \sqrt{\frac{3,45}{6\pi^2}}, \sqrt{\frac{2}{3\pi^2}}$$

gehören.

Die Teilpunkte der Abszissenachse geben die Zahlenwerte

$$Q_1 = 0, \left(\frac{\pi}{4}\right)^2, \left(\frac{2\pi}{4}\right)^2, \left(\frac{3\pi}{4}\right)^2, \pi^2, \left(\frac{5\pi}{4}\right)^2.$$

3. Aus der Fig. 3 geht unmittelbar hervor, dass unter Umständen die Konstruktion „stabil“ sein kann, d.h. dass für jede Vergrößerung der Durchbiegung stets eine Vergrößerung der Kraft P erforderlich ist.

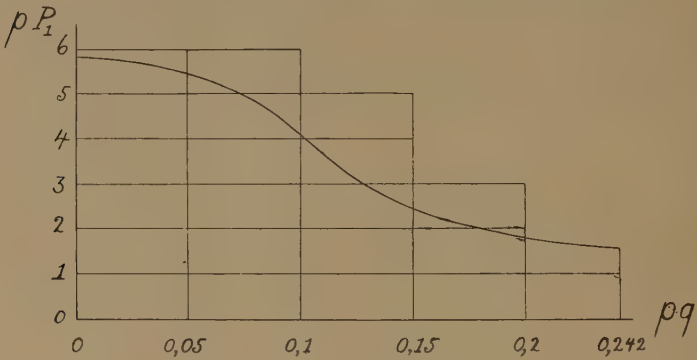


Fig. 4.

Dazu muss die Schleife aus dem (pP_1, Q_1) -Diagramm verschwinden. Stellt man diese Forderung analytisch auf, so findet man als Grenzwert

$$\text{für } (pq): \sqrt{\frac{3.45}{6\pi^2}}.$$

4. Wie schon unter 1. bemerkt wurde, haben wir uns bis jetzt auf den symmetrischen Deformationszustand beschränkt.

Es ist aber auch eine unsymmetrische Ausbiegung möglich, und zwar dann, wenn die Kraft Q die zweite Knickkraft des (gerade gedachten) Stabes übersteigt.

Es wäre dies natürlich auf die Weise nachzurechnen, dass man für jede Stabhälfte die Gleichung der elastischen Linie aufstellt, und unter Verzicht auf die Symmetriebedingung, den glatten Verlauf sowohl der Durchbiegung selbst als ihrer Ableitung in den Punkt $x=0$ fordert. Es wird dann vom Betrage der dazu erforderlichen Energie abhängig sein, unter welchen Umständen die unsymmetrische Durchbiegung sich fürs erste Mal auszubilden vermag.

Ein weit anschaulicheres Bild des hier genannten Vorganges erhält man aber, indem man bedenkt, dass im Augenblicke in welchem Q gleich der zweiten Eulerschen Knickkraft wird, sich auf der bereits vorhandenen Durchbiegung eine andere \sim -förmige superponieren kann, für deren Ausbildung keine Vergrößerung von Q notwendig ist, so dass von diesem Augenblicke an eine weitere, jedoch unsymmetrische Deformation bei konstantem Q eintritt.

Das (pP_1, Q_1) -Diagramm muss also rechts von der Geraden $Q_1 = \pi^2$ begrenzt werden.

Mathematics. — *Skew Correlation between Three and More Variables*, II. By Prof. M. J. VAN UVEN. (Communicated by Prof. A. A. NIJLAND).

(Communicated at the meeting of May 25, 1929).

We may still apply the method hitherto followed, when there is no linear correlation between the original variables x_1, x_2, x_3 appearing in the given frequency distribution **A**, but when linear correlation can be found between the (unimodular) variables t_1, t_2, t_3 , t_a being a function of only x_a ($a = 1, 2, 3$).

Considering, in particular, $t_a \{x_a\}$ as an ever increasing one-valued function of x_a ($a = 1, 2, 3$)¹, $s_a(k_a)$ (**B^a**) gives the probability of $x_a < x_a(k_a)$. Thus the equation **B^a** associates a value $z_a(k_a)$ with $x_a(k_a)$, and we obtain a series of $\nu_a - 1$ empirical values of the function $z_a \{x_a\}$.

Likewise $\sigma_{b;a}(k_a - \frac{1}{2}, k_b)$ (**B(b; a)**) furnishes the probability of $[x_b < x_b(k_b)$, being given: $x_a(k_a - 1) < x_a < x_a(k_a)$]. Hence the equation **B(b; a)** joins a value $\zeta_{b;a}(k_a - \frac{1}{2}, k_b)$ to the set $x_a(k_a - \frac{1}{2}), x_b(k_b)$, and we obtain a series of empirical values of the function $\zeta_{b;a} \{x_a, x_b\}$.

As x_a itself is to be considered as a function of z_a , we may also conceive $\zeta_{b;a}$ as a function of z_a and z_b .

Now z_a is proportional to t_a , so that we (cf 13) may put **9ter (b; a)** into the form:

$$\zeta_{b;a} = \frac{-A_{ba} \cdot \left(\frac{A_{aa}}{A}\right)^{1/2} \cdot z_a + A_{aa} \cdot \left(\frac{A_{bb}}{A}\right)^{1/2} \cdot z_b}{\sqrt{A_{aa}}} = \left. \begin{aligned} &= \frac{-A_{ba} \cdot z_a + \sqrt{A_{aa} A_{bb}} \cdot z_b}{\sqrt{A}} = -\cot \omega_c \cdot z_a + \frac{1}{\sin \omega_c} \cdot z_b \end{aligned} \right\} \text{9 quarter (b; a)}$$

Hence $\zeta_{b;a}$ appears to be a linear function of z_a and z_b .

Finally $S_c(k_a - \frac{1}{2}, k_b - \frac{1}{2}, k_c)$ (**B(c; ba)**) gives the probability of $[x_c < x_c(k_c)$, being given: $x_a(k_a - 1) < x_a < x_a(k_a), x_b(k_b - 1) < x_b < x_b(k_b)]$. Thus the equation **B(c; ba)** associates a value $Z_c(k_a - \frac{1}{2}, k_b - \frac{1}{2}, k_c)$ with the set $x_a(k_a - \frac{1}{2}), x_b(k_b - \frac{1}{2}), x_c(k_c)$. This furnishes us a set of empirical values of the function $Z_c \{x_1, x_2, x_3\}$. As x_a depends only on z_a , Z_c is also to be considered as a function of all three variables z_1, z_2, z_3 .

¹) The limiting agreement that $t \{x\}$ shall be monotone (increasing) is not necessary, but only desirable from a practical point of view and can in certain cases be dropped. (See: M. J. VAN UVEN, *Scheeve Frequentiekrommen*, Versl. K. A. v. W. 25, p. 709, *Skew Frequency Curves*, Proceed. K. Ak. v. Wet. Amsterdam, Vol. 19, p. 670).

In virtue of

$$Z_c = \lambda_{ca} \cdot t_a + \lambda_{bc} \cdot t_b + t_c = \left. \begin{aligned} &= \frac{\lambda_{ca} \sqrt{A_{aa}} \cdot z_a + \lambda_{bc} \sqrt{A_{bb}} \cdot z_b + \sqrt{A_{cc}} \cdot z_c}{\sqrt{A}} \end{aligned} \right\} \text{9 quater (c; ba)}$$

Z_c is a linear function of z_1, z_2, z_3 .

In constructing empirically the functions $\zeta_{b;a}$ and Z_c it is necessary to determine the required mean values as exactly as possible.

Now the values of the functions $\zeta_{b;a}$, Z_c , which correspond to the sets of class-limits $x_a(k_a)$, and to the associated values $z_a(k_a)$, are to be calculated by interpolation. If these calculations are made correctly, and if the conditions that the unimodular variables t_1, t_2, t_3 are pure functions of x_1, x_2, x_3 respectively, are really fulfilled, then it must appear, that the functional values $z_a(k_a)$, $\zeta_{b;a}(k_a, k_b)$, $Z_c(k_a, k_b, k_c)$, corresponding to $x_a(k_a)$, $x_b(k_b)$, $x_c(k_c)$, satisfy the two conditions **Ia** and **Ib**. Moreover it must appear that the three magnitudes γ_{ab} , computed from **Ebis**, are constant, that is to say: that

$$\gamma_{ab} = \frac{A_{ab}}{Q_{ab}^2} = \text{constant } (a, b = 1, 2, 3) \quad \text{II}$$

Inversely, when the conditions

$$\left. \begin{aligned} z_a^2 + \zeta_{b;a}^2 &= z_b^2 + \zeta_{a;b}^2 (= q_{ab}^2), & \text{Ia} \\ Z_c^2 &= H\{z, \zeta\} - q_{ab}^2, & \text{Ib} \\ \gamma_{ab} &= \frac{A_{ab}}{Q_{ab}^2} = \text{constant}, & \text{II} \end{aligned} \right\} (a, b, c = 1, 2, 3)$$

are fulfilled, we may conclude, that *linear correlation* exists between the unimodular variables t_1, t_2, t_3 , determined by

$$t_a = \frac{z_a}{\sin \psi_a} = \left(\frac{\Gamma_{aa}}{\Gamma} \right)^{1/2} \cdot z_a \quad (a = 1, 2, 3) \quad \text{J}$$

t_a being (in virtue of $\psi_a = \text{const.}$) a pure function of x_a .

If t_a is a pure function of x_a ($a = 1, 2, 3$), each arrangement $z_a, \zeta_{b;a}, Z_c$ associates with the set x_1, x_2, x_3 the same point $P(t_1, t_2, t_3)$ in the same (skew) system of coordinates t_1, t_2, t_3 . Hence we obtain on the unity-sphere for each set x_1, x_2, x_3 the same spherical triangle (Φ) of reference, thus also the same polar triangle (Ω). In this case the (total) coefficients of correlation of $t_1\{x_1\}$, $t_2\{x_2\}$, $t_3\{x_3\}$ are the cosines of the (constant) sides of the polar triangle:

$$\gamma_{23} = \cos \omega_1, \quad \gamma_{31} = \cos \omega_2, \quad \gamma_{12} = \cos \omega_3.$$

If, in particular, t_a is a linear function of x_a , $t_a = h_a(x_a - \bar{x}_a)$, the

function z_a , too, will be a linear function of x_a , the function $\zeta_{b;a}$ will be linear in x_a and x_b , Z_c linear in x_1, x_2, x_3 . Then the original variables x_1, x_2, x_3 themselves are linearly correlated.

This statement furnishes us a rather reliable test of the linearity of the correlation between x_1, x_2, x_3 .¹⁾

Since no empirical frequency distribution is *rigorously* conform to any ideal theoretical probability scheme, and since we have to reckon with several sources of inaccuracy, as well in calculating mean values (such as $\zeta_{2;1}(k_1 - \frac{1}{2}, k_2)$, $Z_3(k_1 - \frac{1}{2}, k_2 - \frac{1}{2}, k_3)$) as in interpolating (e.g. to compute $\zeta_{2;1}(k_1, k_2)$, $Z_3(k_1, k_2, k_3)$), we cannot reasonably expect, that even in the case $t_a \{x_a\}$ the conditions Ia, b and II will be satisfied *exactly*. We shall have to content ourselves with an *approximate* validity of these equations. Only when the quotients $q_{a,b} : q_{b;a}$, $Z_c^2 : (H\{z, \zeta\} - Q_{ab}^2)$ and the variables γ_{ab} show some obvious functional dependency on x_1, x_2, x_3 , should we be obliged to drop the supposition $t_a \{x_a\}$ ($a = 1, 2, 3$).

If the condition II is not fulfilled, that is to say: if the values of $\gamma_{bc} = \cos \omega_a$ computed for the different sets $x_1(k_1), x_2(k_2), x_3(k_3)$, are *unequal*, so that $\omega_1, \omega_2, \omega_3$ are *variable magnitudes*, then we may introduce a constant polar triangle ($\bar{\Omega}$) with sides $\bar{\omega}_1, \bar{\omega}_2, \bar{\omega}_3$. In order to keep in touch, as much as possible, with the values $\omega_1, \omega_2, \omega_3$ really found: it is preferable to choose for $\bar{\omega}_a$ an *average* value of ω_a . We may obtain such average values by taking the averages of

$$M_1 = \text{tg } \omega_1 = \frac{B_{23}}{A_{23}}, \quad M_2 = \text{tg } \omega_2 = \frac{B_{31}}{A_{31}}, \quad M_3 = \text{tg } \omega_3 = \frac{B_{12}}{A_{12}},$$

according to the precept we have formerly given in S. C. I. b (Dutch text p. 976, English text p. 929).

A_{23} and B_{23} are merely functions of x_2 and x_3 . So, in averaging M_1 , the frequency distribution is to be treated as a two-dimensional one, its frequencies being $Y'(k_2, k_3) = \sum_{i_1=1}^{v_1} Y(i_1, k_2, k_3)$. Hence the "weights" introduced in averaging $M_1 = \text{tg } \omega_1$ are built up of these two-dimensional frequencies $Y'(k_2, k_3)$. Likewise for averaging M_2 and M_3 .

From the averages $\bar{\omega}_a$ ($a = 1, 2, 3$) we compute the corresponding arcs $\bar{\varphi}_a$ and $\bar{\psi}_a$ ($a = 1, 2, 3$).

Then we put, guided by 9bis,

$$\left. \begin{aligned} z_1 &= \sin \bar{\psi}_1 \cdot T_1, \\ \zeta_{2;1} &= -\sin \bar{\varphi}_2 \cos \bar{\omega}_3 \cdot T_1 + \sin \bar{\varphi}_1 \cdot T_2, \\ Z_3 &= \cos \bar{\varphi}_2 \cdot T_1 + \cos \bar{\varphi}_1 \cdot T_2 + T_3. \end{aligned} \right\} \quad . \quad . \quad 32 \quad \left\{ \begin{array}{l} (1) \\ (2; 1) \\ (3; 2 1) \end{array} \right.$$

¹⁾ See the footnote further on, preceding equat. J in the treatment of n variables.

or

$$T_3 = \left\{ \frac{\cos \varphi_2 \sin \bar{\varphi}_1 + \cos \bar{\varphi}_1 \sin \varphi_2 \cos \omega_3}{\sin \varphi_1} - \frac{(\cos \bar{\varphi}_2 \sin \bar{\varphi}_1 + \cos \bar{\varphi}_1 \sin \bar{\varphi}_2 \cos \bar{\omega}_3) \sin \psi_1}{\sin \varphi_1 \sin \psi_1} \right\} t_1 - \frac{\sin \varphi_1 \cos \bar{\varphi}_1 - \cos \varphi_1 \sin \bar{\varphi}_1}{\sin \varphi_1} t_2 + t_3.$$

We now have in the "average" spherical triangle $\bar{\Phi}_1 \bar{\Phi}_2 \bar{\Phi}_3$:

$$\begin{aligned} \cos \bar{\varphi}_2 \sin \bar{\varphi}_1 + \cos \bar{\varphi}_1 \sin \bar{\varphi}_2 \cos \bar{\omega}_3 &= \cos \bar{\varphi}_2 \sin \bar{\varphi}_1 - \cos \bar{\varphi}_1 \sin \bar{\varphi}_2 \cos \bar{\Phi}_3 = \\ &= \sin \bar{\varphi}_3 \cos \bar{\Phi}_2 = -\sin \bar{\varphi}_3 \cos \bar{\omega}_2; \end{aligned}$$

hence the second term in the coefficient of t_1 becomes:

$$+ \frac{\sin \bar{\varphi}_3 \cos \bar{\omega}_2}{\sin \varphi_1 \sin \psi_1} \cdot \sin \psi_1 = \frac{\sin \bar{\varphi}_3 \cos \bar{\omega}_2}{\sin \varphi_1 \sin \bar{\varphi}_3 \sin \bar{\omega}_2} \cdot \sin \psi_1 = \frac{\cot \bar{\omega}_2}{\sin \varphi_1} \cdot \sin \psi_1.$$

Thus we obtain, by $t_a = \frac{z_a}{\sin \psi_a}$ ($a = 1, 2, 3$),

$$T_3 = \left(\frac{\cos \varphi_2 \sin \bar{\varphi}_1 + \cos \bar{\varphi}_1 \sin \varphi_2 \cos \omega_3}{\sin \varphi_1 \sin \psi_1} + \frac{\cot \bar{\omega}_2}{\sin \varphi_1} \right) z_1 - \left. \begin{aligned} & - \frac{\sin (\varphi_1 - \bar{\varphi}_1)}{\sin \varphi_1 \sin \psi_2} z_2 + \frac{1}{\sin \psi_3} z_3. \end{aligned} \right\} \quad 35$$

The first term in the coefficient of z_1 can be interpreted geometrically as follows:

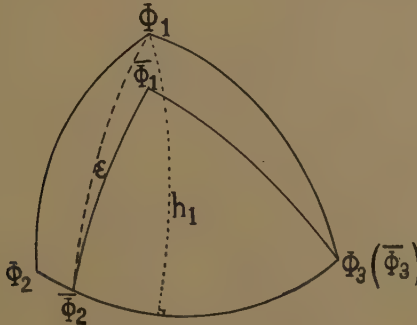


fig. 4

We locate the "average" spherical triangle so, that $\bar{\Phi}_3$ coincides with Φ_3 , and that $\bar{\Phi}_2 \bar{\Phi}_3$ falls along $\Phi_2 \Phi_3$ (fig. 4).

Putting

$$\angle \Phi_1 \bar{\Phi}_2 \bar{\Phi}_1 = \varepsilon,$$

we have in $\triangle \Phi_1 \bar{\Phi}_2 \bar{\Phi}_3$:

$$\cos \varphi_2 \sin \bar{\varphi}_1 - \cos \bar{\varphi}_1 \sin \varphi_2 \cos \bar{\Phi}_3 = \sin \bar{\Phi}_2 \Phi_1 \cdot \cos \bar{\Phi}_3 \bar{\Phi}_2 \Phi_1,$$

or

$$\begin{aligned} \cos \varphi_2 \sin \bar{\varphi}_1 + \cos \bar{\varphi}_1 \sin \varphi_2 \cos \omega_3 &= \frac{\sin h_1}{\sin (\bar{\Phi}_2 + \varepsilon)} \cos (\bar{\Phi}_2 + \varepsilon) = \\ &= \sin \psi_1 \cot (\bar{\Phi}_2 + \varepsilon) = -\sin \psi_1 \cot (\omega_2 - \varepsilon). \end{aligned}$$

Hence the coefficient of z_1 becomes:

$$\frac{1}{\sin \varphi_1} \{-\cot (\omega_2 - \varepsilon) + \cot \omega_2\} = \frac{-\sin \varepsilon}{\sin \varphi_1 \sin \omega_2 \sin (\omega_2 - \varepsilon)} = \frac{-\sin \varepsilon}{\sin \psi_3 \sin (\omega_2 - \varepsilon)}.$$

Thus we find for T_3 :

$$T_3 = \frac{-\sin \varepsilon}{\sin \psi_3 \sin (\omega_2 - \varepsilon)} z_1 - \frac{\sin (\varphi_1 - \bar{\varphi}_1)}{\sin \varphi_1 \sin \psi_2} z_2 + \frac{1}{\sin \psi_3} z_3. \quad 35bis$$

So we have together:

$$\left. \begin{aligned} T_1 &= \frac{1}{\sin \psi_1} z_1, \\ T_2 &= \frac{\sin (\omega_3 - \bar{\omega}_3)}{\sin \bar{\psi}_2 \sin \omega_3} z_1 + \frac{1}{\sin \varphi_1 \sin \omega_3} z_2 \\ T_3 &= \frac{-\sin \varepsilon}{\sin \psi_3 \sin (\omega_2 - \varepsilon)} z_1 - \frac{\sin (\varphi_1 - \bar{\varphi}_1)}{\sin \varphi_1 \sin \psi_2} z_2 + \frac{1}{\sin \psi_3} z_3 \end{aligned} \right\} \quad K$$

where ε is determined by

$$\cot (\omega_2 - \varepsilon) = -\frac{\sin \bar{\varphi}_1 \cos \varphi_2 + \cos \bar{\varphi}_1 \sin \varphi_2 \cos \omega_3}{\sin \psi_1}.$$

In this way we have constructed three variables T_1, T_2, T_3 , which are *linearly* correlated, having the (total) coefficients of correlation:

$$\bar{\gamma}_{23} = \cos \bar{\omega}_1, \quad \bar{\gamma}_{31} = \cos \bar{\omega}_2, \quad \bar{\gamma}_{12} = \cos \bar{\omega}_3.$$

T_1 is a function of only z_1 , thus a pure function of x_1 .

Since $\omega_3 = \arctg \frac{B_{12}}{A_{12}}$ is built up out of $z_1, z_2, \zeta_{2,1}, \zeta_{1,2}$, z_1 depending only on x_1 , z_2 only on x_2 , $\zeta_{2,1}$ and $\zeta_{1,2}$ only on x_1 and x_2 , we recognize ω_3 to be a function only of x_1 and x_2 . Thus:

T_2 is a function only of x_1 and x_2 $\left(\frac{\partial T_2}{\partial x_3} = 0 \right)$.

T_3 however is a function of all three variables x_1, x_2, x_3 .

Hence:

If the conditions Ia and Ib are fulfilled, but II is not, we may, by introducing the constant (average) magnitudes

$\overline{\omega_1}, \overline{\omega_2}, \overline{\omega_3}$, establish a linear correlation between $T_1\{x_1\}$, $T_2\{x_1, x_2\}$, $T_3\{x_1, x_2, x_3\}$. Then the (total) coefficients of correlation are $\gamma_{23} = \cos \omega_1$, $\gamma_{31} = \cos \omega_2$, $\gamma_{12} = \cos \omega_3$.

If, the magnitudes ω_1 and ω_2 being variable, the magnitude $\omega_3 = \arctg \frac{B_{12}}{A_{12}}$ is found to be constant, then we naturally choose this constant value for $\overline{\omega_3}$ (fig. 5), whence $\omega_3 - \overline{\omega_3} = 0$.

In this case T_2 becomes a pure function of x_2 .

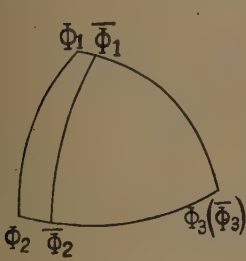


fig.5

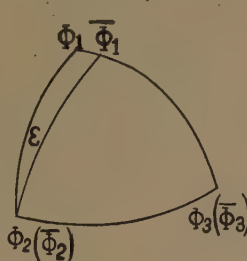


fig.6

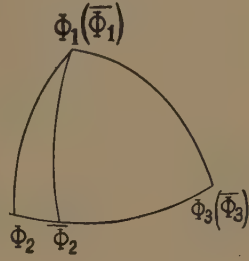


fig.7

If it is found that not only ω_3 , but also φ_1 is constant (fig. 6), the expression

$$\cos \varphi_1 = \frac{\cos \omega_2 \cos \omega_3 - \cos \omega_1}{\sin \omega_2 \sin \omega_3} = \frac{A_{31} A_{12} Q_{23}^2 - A_{23} Q_{31}^2 Q_{12}^2}{B_{31} B_{12} Q_{23}^2}$$

turning out to take the same value for each set $x_1(k_1)$, $x_2(k_2)$, $x_3(k_3)$, then we have also

$$\sin \varphi_2 = \sin \omega_3 \sin \varphi_1 = \text{constant.}$$

We now obtain (see fig. 6):

$$\varepsilon = \Phi_2 - \overline{\Phi_2} = -(\omega_2 - \overline{\omega_2}) \quad , \quad \overline{\omega_2} - \varepsilon = \omega_2.$$

In this case the expression 35bis for T_3 gets rid of its term with z_2 , and is reduced to

$$T_3 = \frac{\sin(\omega_2 - \overline{\omega_2})}{\sin \varphi_3 \sin \omega_2} z_1 + \frac{1}{\sin \varphi_3} z_3.$$

Here ω_2 is a function only of z_1 and z_3 ; so $\sin \varphi_3 (= \sin \varphi_1 \sin \omega_2)$ is. Therefore: $\omega_3 = \text{const.}$ and $\varphi_1 = \text{const.}$ furnishes $T_1\{x_1\}$, $T_2\{x_2\}$, $T_3\{x_1, x_3\}$.

If, besides ω_3 , also φ_2 turns out to be constant, the expression

$$\cos \varphi_2 = \frac{A_{12} A_{23} Q_{31}^2 - A_{31} Q_{12}^2 Q_{23}^2}{B_{12} B_{23} Q_{31}^2}$$

taking the same value for each set $x_1(k_1), x_2(k_2), x_3(k_3)$, then $\varepsilon = 0$ (see fig. 7), so that T_3 drops its term with z_1 , and is reduced to

$$T_3 = \frac{-\sin(\varphi_1 - \overline{\varphi_1})}{\sin \varphi_1 \sin \psi_2} z_2 + \frac{1}{\sin \psi_3} z_3.$$

Here $\sin \psi_3 = \sin \varphi_2 \sin \omega_1 \{x_2, x_3\}$ is a function only of x_2 and x_3 ; however the coefficient of z_2 still depends on all the variables x_1, x_2, x_3 . Hence in this case T_3 is still a function of all three variables x_a .

By interchanging the subscripts we may — in the same manner — arrive at analogous relations of dependency.

We may observe, that we have computed the elements of the spherical triangle of reference exclusively by means of **E**, hence out of the magnitudes $z_a, \zeta_{b;a}$. So we have only used these magnitudes, which are much more accurate than the magnitudes Z_c , ¹ because, for calculating Z_c , we have much more to do with mean values (e.g. $z_a(k_a - \frac{1}{2})$) and with interpolated values (e.g. $Z_c(k_1, k_2, k_3)$), ² because the magnitudes Z_c (see **B(3;21)**) are computed from — generally small — one-dimensional frequency sums.

If **Ia** is satisfied, but **Ib** is not, then the 6 triplets $z_a, \zeta_{b;a}, Z_c$ still join to each set $x_1(k_1), x_2(k_2), x_3(k_3)$ one and the same image point $\Pi(k_1, k_2, k_3)$ on the unity-sphere (see fig. 3), the 3 expressions $r_{ab}^2 = q_{ab}^2 + Z_c^2$ giving however values for r^2 different from the value of $H\{z, \zeta\}$ as it is deduced solely from the magnitudes $z_a, \zeta_{b;a}$. We may now introduce new magnitudes Z'_1, Z'_2, Z'_3 , which do satisfy **Ib**, in other words: we put:

$$Z_c'^2 = H\{z, \zeta\} - q_{ab}^2 \quad (c = 1, 2, 3) \quad \quad 36$$

and consider these Z'_c as "adjusted" values of Z_c . So we replace the empirical triplets $z_a, \zeta_{b;a}, Z_c$, computed from the *given* frequency distribution, by the triplets $z_a, \zeta_{b;a}, Z'_c$. By computing back the frequency distribution corresponding to the *adjusted* triplets, this frequency distribution will appear to be somewhat different from the given one. Then we must judge whether the discrepancy thus found between the given and the computed frequency distribution may be considered as a small accidental deviation.

We are inclined to adjust in the first place the magnitudes Z_c , these being subject to the greatest uncertainty. It is, on the other hand, the great uncertainty of Z_c which makes the frequency distribution rather insensible to an alteration of Z_c .

When we, nevertheless, in computing back the frequency distribution, desire to get back *exactly* the *given* frequencies, we may succeed by keeping one of the magnitudes Z_c , for instance Z_3 , unaltered.¹⁾ Then

¹⁾ We shall preferably keep that magnitude Z_c , which satisfies **Ib** best

enables us to compute the new value q'_{23} of q_{23} , viz.:

$$q'_{23} = \frac{z_2^2 - 2 \cos \omega'_1 \cdot z_2 z_3 + z_3^2}{\sin^2 \omega'_1} \quad 41$$

Putting:

$$q'_{23} = q_{23}^2 + \delta, \quad 42$$

the equations

$$\zeta'_{2;3} = \zeta_{2;3}^2 + \delta, \quad \zeta'_{3;2} = \zeta_{3;2}^2 + \delta \quad 43$$

furnish the adjusted values $\zeta'_{2;3}$ and $\zeta'_{3;2}$ of $\zeta_{2;3}$ and $\zeta_{3;2}$.

We naturally choose the average value ω'_1 of the new values ω'_1 for the constant ω_1 in the formulae **K** for T_1, T_2, T_3 . Here we use the *adjusted* spherical triangles (Φ') and (Ω') , determined by the unaltered sides ω_2 and ω_3 , and by the adjusted side ω'_1 . This latter must be computed from **37, 38, 39bis, 40**, thus according to the scheme:

$$\left. \begin{aligned} r'^2 &= r_{12}^2 = q_{12}^2 + Z_3^2, \\ Z_2'^2 &= r'^2 - q_{31}^2, \\ \operatorname{tg} \varphi'_1 &= \frac{Z_2' \zeta_{2;1} + Z_3 \zeta_{3;1}}{Z_2' Z_3 - \zeta_{3;1} \zeta_{2;1}}, \\ \cos \omega'_1 &= \cos \omega_2 \cos \omega_3 - \sin \omega_2 \sin \omega_3 \cos \varphi'_1 \end{aligned} \right\} \text{L}$$

If none of the conditions **Ia, b, II** is satisfied, then some of the magnitudes $z_a, \zeta_{b;a}$ must also be adjusted. Unless we desire, intentionally, to keep at least one of the magnitudes Z_c , we prefer to determine $\omega_1, \omega_2, \omega_3$ again by the equations **Ebis**, in which A_{ab} and B_{ab} are constructed out of the *unadjusted* values $z_{\bar{a}}, z_b, \zeta_{b;\bar{a}}, \zeta_{a;b}$.

Now we must make $q_{b;a}$ agree with $q_{a;b}$.

Referring to S. C. II, p. 408, we observe that the most preferable methods of adjustment are the following two:

a.: we keep z_a and z_b , derive ω_c from **Ebis**, and adjust the values $\zeta_{b;a}$ and $\zeta_{a;b}$ to the values $\zeta'_{b;a}$ and $\zeta'_{a;b}$, which are, in virtue of **9ter (b; a)** determined by

$$\zeta'_{b;a} = \frac{z_b - \cos \omega_c \cdot z_a}{\sin \omega_c}, \quad \zeta'_{a;b} = \frac{z_a - \cos \omega_c \cdot z_b}{\sin \omega_c} \quad 44$$

(see fig. 8).

So we adjust $q_{b;a}$ and $q_{a;b}$ to $q'_{b;a} = q'_{a;b} = q'_{ab}$, determined by

$$q'^2_{ab} = z_a^2 + \zeta'^2_{b;a} = z_b^2 + \zeta'^2_{a;b} = \frac{z_a^2 - 2 \cos \omega_c \cdot z_a z_b + z_b^2}{\sin^2 \omega_c} \quad . . . 45$$

Then the function $r^2 = H\{z, \zeta\}$, being (by **31**) built up of the magni-

tudes z_a and ω_a ($a = 1, 2, 3$) may be computed immediately by means of the values $\omega_1, \omega_2, \omega_3$ calculated from **Ebis**.

So we have evidently:

$$H\{z, \zeta'\} = H\{z, \zeta\}.$$

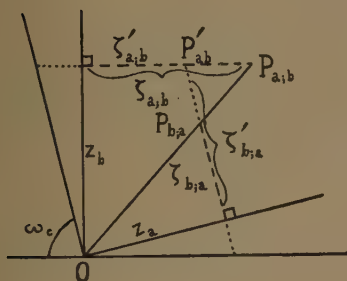


fig.8

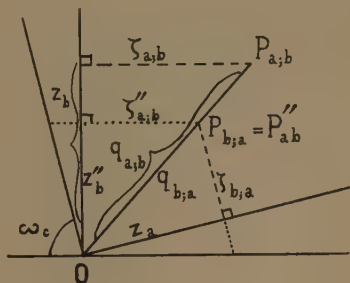


fig.9

Then the magnitudes Z_c are adjusted into Z'_c according to 36.

The spherical triangles (Φ) and (Ω) remaining unaltered, we derive the unimodular, linearly correlated variables T_1, T_2, T_3 still from the same equations **K**, we formerly constructed.

In computing back the frequency distribution out of one of the triplets $z_a, \zeta'_{b;a}, Z'_c$, we must be prepared to find deviations from the original frequency distribution. The advantage of this method is, however, that we make as much use as possible of the magnitudes z_1, z_2, z_3 , which are the most accurate ones.

b. We keep z_a and $\zeta_{b;a}$, thus also $q_{b;a}^2 = z_a^2 + \zeta_{b;a}^2$, and derive ω_c still from **Ebis** (fig. 9). The magnitude z_b however must now be replaced by z''_b , which is, in virtue of **9ter** (**b; a**), determined by

$$z''_b = \cos \omega_c \cdot z_a + \sin \omega_c \cdot \zeta_{b;a} \quad . \quad . \quad . \quad \mathbf{M}$$

By means of **E** we may transform this expression into:

$$z''_b = \frac{z_a A_{ab} + \zeta_{b;a} B_{ab}}{q_{b;a} \cdot q_{a;b}} = \frac{z_a (z_a z_b - \zeta_{b;a} \zeta_{a;b}) + \zeta_{b;a} (z_a \zeta_{a;b} + z_b \zeta_{b;a})}{q_{b;a} \cdot q_{a;b}} = \frac{z_b \cdot q_{b;a}^2}{q_{b;a} \cdot q_{a;b}},$$

or

$$z''_b = \frac{q_{b;a}}{q_{a;b}} \cdot z_b \quad . \quad . \quad . \quad \mathbf{Mb\text{is}}$$

Therefore, if we wish to keep, for instance, z_1 and $\zeta_{2;1}$, we must replace z_2 by $z''_2 = \frac{q_{2;1}}{q_{1;2}} \cdot z_2$, and substitute this value z''_2 for z_2 in the equations **K**. The method (*b*) is to be followed, if we desire, intentionally, to get back the original frequency distribution out of one of the triplets. In this case we have, of course, to leave also Z_c (i.e. Z_3)

unaltered, and to apply the corresponding method of adjustment, however on the understanding, that we must take for r^2 the value:

$$r''^2 = r_{2;1}^2 = q_{2;1}^2 + Z_3^2 = z_1^2 + \zeta_{2;1}^2 + Z_3^2, \quad 46$$

so that also the values of $Z'_2, \varphi'_1, \omega'_1$ turn out to be different from those derived from L.

If we desire to keep $\zeta_{3;1}$ and $\zeta_{1;3}$, we must, while retaining ω_2 , replace these magnitudes, according to 44, by

$$\zeta''_{3;1} = \frac{z_3 - \cos \omega_2 \cdot z_1}{\sin \omega_2}, \quad \zeta''_{1;3} = \frac{z_1 - \cos \omega_2 \cdot z_3}{\sin \omega_2} \quad . . . 47$$

Then we must take for q_{31}^2 (see 41):

$$q_{31}''^2 = \frac{z_3^2 - 2 \cos \omega_2 \cdot z_3 z_1 + z_1^2}{\sin^2 \omega_2} \quad 48$$

So we obtain for Z_2 the adjusted value Z''_2 , determined by

$$Z_2''^2 = r''^2 - q_{31}''^2 \quad 49$$

By means of the value $\zeta''_{3;1}$, found from 47, and the value Z''_2 , derived from 49, we now compute the adjusted value φ''_1 from

$$\operatorname{tg} \varphi''_1 = \frac{Z_2'' \zeta_{2;1} + Z_3 \zeta_{3;1}}{Z_2'' Z_3 - \zeta_{3;1} \zeta_{2;1}} \quad 50$$

At last we find the adjusted value ω''_1 from

$$\cos \omega''_1 = \cos \omega_2 \cos \omega_3 - \sin \omega_2 \sin \omega_3 \cos \varphi''_1 \quad 51$$

Then we determine the average value $\bar{\omega}''_1$ of this adjusted value ω''_1 , after which we substitute this value $\bar{\omega}''_1$ for the constant $\bar{\omega}_1$ in the formulae K. Hence, in the actual case ($z_1, \zeta_{2;1}, Z_3$ being kept) the formulae K are altered in such a way that we replace z_2 by z''_2 (determined by M (Mbis)) and $\bar{\omega}_1$ by $\bar{\omega}''_1$ (determined by 46–51). So the adjustment is to be effectuated according to the scheme:

$$\left. \begin{aligned} z''_2 &= \cos \omega_3 \cdot z_1 + \sin \omega_3 \cdot \zeta_{2;1} = \frac{q_{2;1}}{q_{1;2}} \cdot z_2 \\ r''^2 &= r_{2;1}^2 = z_1^2 + \zeta_{2;1}^2 + Z_3^2 \\ \zeta''_{3;1} &= \frac{z_3 - \cos \omega_2 \cdot z_1}{\sin \omega_2} \\ q_{31}''^2 &= \frac{z_3^2 - 2 \cos \omega_2 \cdot z_3 z_1 + z_1^2}{\sin^2 \omega_2} \\ Z_2''^2 &= r''^2 - q_{31}''^2 \\ \operatorname{tg} \varphi''_1 &= \frac{Z_2'' \zeta_{2;1} + Z_3 \zeta_{3;1}}{Z_2'' Z_3 - \zeta_{3;1} \zeta_{2;1}} \\ \cos \omega''_1 &= \cos \omega_2 \cos \omega_3 - \sin \omega_2 \sin \omega_3 \cos \varphi''_1 \end{aligned} \right\} \quad N$$

Of course the other elements φ_a, ψ_a of the spherical triangles occurring in **K**, are to be recomputed from $\omega''_1, \omega_2, \omega_3$. Thereby they undergo alteration, and so do the constants φ_a, ψ_a derived from $\omega''_1, \omega_2, \omega_3$.

Summary of the Treatment of Skew Correlation between Three Variables:

From the given frequency distribution **A** the magnitudes $z_a, \zeta_{b;a}, Z_c$ are calculated by means of **B**.

The equations **C** (**Cbis**), **D**, **E** (**Ebis**), **F**, **G**, **H** define the magnitudes $q_{b;a}, Q_{ab}, A_{ab}, B_{ab}, M_{ab}, \gamma_{ab}, r^2 = H\{z, \zeta\}$, by means of which we can formulate the conditions **Ia**, **b**, **II**:

$$q_{b;a} = q_{a;b} (= q_{ab}) \quad (a, b = 1, 2, 3) \quad \dots \quad \text{Ia}$$

$$Z_c^2 = H\{z, \zeta\} - q_{ab}^2 \quad (c = 1, 2, 3) \quad \dots \quad \text{Ib}$$

$$\frac{\sqrt{1 - \gamma_{ab}^2}}{\gamma_{ab}} = M_{ab} = \frac{B_{ab}}{A_{ab}} = \text{constant} \quad \dots \quad \text{II}$$

If both **Ia**, **b** and **II** are satisfied for each set $x_1(k_1), x_2(k_2), x_3(k_3)$, there exists linear correlation between the unimodular variables $t_1\{x_1\}, t_2\{x_2\}, t_3\{x_3\}$, determined by the equations **J**, the total coefficients of correlation being $\gamma_{23}, \gamma_{31}, \gamma_{12} \left(\frac{\gamma_{ab}}{A_{ab}} > 0 \right)$.

If **Ia**, **b** are satisfied, but **II** is not, then we can establish linear correlation between the (unimodular) variables $T_1\{x_1\}, T_2\{x_1, x_2\}, T_3\{x_1, x_2, x_3\}$ given by the equations **K**, the total coefficients of correlation being $\gamma_{23}, \gamma_{31}, \gamma_{12}$.

If **Ib** is not satisfied, then we may, by abandoning — if necessary — all the magnitudes Z_c , keep the variables $T_1\{x_1\}, T_2\{x_1, x_2\}, T_3\{x_1, x_2, x_3\}$ determined by **K**. If, however, we insist upon keeping Z_3 intact, then either ω_1 or ω_2 must be altered. When we keep ω_2 , the magnitude ω_1 must be adjusted to the magnitude ω'_1 , to be computed by means of the equations **L**. Then this ω'_1 and its average $\bar{\omega}'_1$ take the place of ω_1 and $\bar{\omega}_1$ in the formulae **K**.

If even **Ia** is not fulfilled, we may, by abandoning — if necessary — all the magnitudes $\zeta_{b;a}$, but keeping the magnitudes $\omega_1, \omega_2, \omega_3$, computed from **Ebis**, retain, even in this case, the variables $T_1\{x_1\}, T_2\{x_1, x_2\}, T_3\{x_1, x_2, x_3\}$ defined by **K**.

If, on the contrary, we wish to keep $\zeta_{2;1}$ intact, we must replace z_2 by the magnitude z''_2 , determined by **M** (**Mbis**). If we desire to keep not only $\zeta_{2;1}$ but also Z_3 unaltered, we must replace the magnitudes z_2 and ω_1 by the magnitudes z''_2 and ω''_1 determined by **N**, and reconstruct the formulae **K**, using those adjusted values z''_2, ω''_1 and the average $\bar{\omega}''_1$. Then the arcs φ_a, ψ_a ($a = 1, 2, 3$) must first be computed from $\omega''_1, \omega_2, \omega_3$, and their averages φ_a, ψ_a from $\omega''_1, \omega_2, \omega_3$.

(To be continued).

Botany. — *Studies on Limiting Factors in Carbon Dioxide Assimilation.*
By T. H. VAN DEN HONERT. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of March 31, 1928).

The velocity, with which a green plant assimilates CO_2 , depends upon three environmental factors, to wit: CO_2 concentration, light intensity and temperature. In a well-known article F. F. BLACKMAN (1905) has formulated this relation as follows:

"When a process is conditioned as to its rapidity by a number of separate factors, the rate of the process is limited by the pace of the "slowest" factor".

The graphical representation of this is the well-known curve: an ascending line, which represents the assimilation velocity as influenced by the increase of a factor a , which line suddenly and discontinuously becomes horizontal as soon as a velocity is reached, at which a second factor b becomes the limiting factor. The point at which this happens I will call the *transition point* (the point at which there is a transition of limitation by factor a to a limitation by factor b). We will therefore define the transition point as the point at which two factors exert the same influence on the velocity of the process.

Assuming BLACKMAN's formulation to be a true representation of the facts, we may arrive at three different combinations of properties characterising the assimilation process.

The velocity of the process may be:

- | | | |
|---|---|-----------------------------------|
| 1 ^o . Directly proportional to CO_2 concentration, Independent of light intensity, " " temperature ($Q_{10} = 1$). | } | CO_2 "limiting". |
| 2 ^o . Directly proportional to light intensity, Independent of CO_2 concentration, " " temperature ($Q_{10} = 1$). | | light intensity "limiting". |
| 3 ^o . Exponentially increasing with temperature ($Q_{10} = \pm 2$), Independent of CO_2 concentration, " " light intensity. | } | temperature "limiting". |

Physical chemistry cannot account for these three combinations of properties as long as we consider the assimilation to be a *simple* process.

One may look in vain for a simple chemical reaction, which will change its characteristics in such a fundamental way by varying its dominating factors, such as temperature and concentration. The objections of BROWN

and HEISE (1917) against BLACKMAN's formulation are based upon similar considerations. The above mentioned objection disappears, when we consider the assimilation process as a catenary reaction, consisting of at least three distinct consecutive processes. For in a catenary process the velocity with which the final product is formed, is dominated by the *slowest* reaction. These reactions may possess entirely different individual properties, the velocity of the "total" process will have the properties of the reaction, which will be momentarily the slowest.

In this direction WILLSTÄTTER and STOLL (1918), BRIGGS (1920), THODAY (1922) and WARBURG (1920—1924) have been looking for the explanation of the phenomena.

BLACKMAN's formulation has not remained unattacked. Considerable discrepancies have been found by various workers; the above mentioned discontinuous curve was found to be considerably rounded near the transition point. Various other formulations have been given to account for this experimental fact. (BOYSEN JENSEN 1919, HARDER 1921, BENECKE 1921, LUNDEGÅRDH 1924.)

These workers used leaves or even entire plants in their experiments. The individual plastids of a single leaf, however, are in entirely different conditions. When the leaf is illuminated from above, the plastids near the upper surface will receive much more light than those near the lower surface.

Increase in light intensity will create a condition, at which the light is no longer a limiting factor for the plastids near the upper surface. Increasing the light intensity still further, the "transition point" will also be reached for the deeper layers, and finally for the lower surface of the leaf. We may therefore say that, even if BLACKMAN's formulation would hold for each individual plastid, one would still expect for the entire leaf a gradual transition from limitation by light to limitation by temperature or CO_2 . The more the conditions of the plastids are different *inter se*, the more gradual this transition will be and the more the curve will be rounded.

Also the CO_2 concentration needs not to be the same for all plastids (SCHROEDER 1924). Moreover the capricious behaviour of the stomata materially hampers the experiments with CO_2 as limiting factor.

If we want to obtain a true picture, we will have to carry out our experiments in such a way, that *all plastids will be in the same condition as far as CO_2 and light are concerned*. We have recourse in the first place to unicellular organisms as WARBURG (1919) did, using in his experiments the unicellular green alga *Chlorella*.

Because of the very small dimensions of the cells, the CO_2 has only to diffuse over a very short distance to reach the plastid. In view of this fact, WARBURG is of the opinion, that the diffusion process will never hamper the velocity of the assimilation. We will discuss the validity of this assumption later in this paper.

WARBURG, in his experiments on the influence of light intensity, has taken the precaution to use very dilute cell suspensions. With this procedure

he approached the ideal condition of homogeneous environment for all cells.

In my opinion this ideal has not been reached entirely by him. Probably a part of the cells is shaded by the rest.

A second objection to WARBURG's on the whole brilliant method is his use of buffer mixtures in order to vary the CO_2 concentration. The cells have to be exposed to various acidities, which introduces a new complication.

In this paper a method is described in which these two objections are avoided.

The problem may be put as follows :

1^o. Which is the relation in the individual plastid between assimilation velocity on one hand, CO_2 concentration, light intensity and temperature on the other hand ?

2^o. May the assimilation be reduced to a catenary process ?

This is a preliminary account.

Shortly a more extensive account will appear (1928).

Methods.

a. The object.

As experimental object I selected a filamentous alga, belonging to the genus *Hormidium*, isolated from material growing on a garden wall. The alga is easily cultivated in flasks on purely inorganic media. In this case the bacterial development is minimal. The alga has the property to form shiny pellicles, one cell thick, floating on the liquid media. This property has been made use of in the following way.

The algal material, which has to serve for an experiment, is oculated upon the surface of a liquid medium, which is put into a receptacle. This receptacle has a bottom, formed by a glass plate. The walls are formed by an oblong ring of ebonite, a rubber ring serving as a water-tight seal between bottom and wall.

Before starting the experiment, the liquid is siphoned off for the largest part from below the pellicle of algae, which pellicle remains with very little liquid on the glass plate. This glass plate will serve, after removal of the ebonite ring, as the bottom of the assimilation vessel (fig. 1, 15).

b. Apparatus.

The technical requirements of the method are the following. In the assimilation vessel we must be able to vary or to keep constant CO_2 concentration, as well as light intensity and temperature individually and arbitrarily. The CO_2 concentration in the assimilation vessel has to be determined to .001 % accurate. This concentration has to be the same in all parts of the vessel. Production and consumption of CO_2 (respiration and assimilation) must be determined accurately.

The CO_2 determinations were carried out with a slightly modified KROGH's apparatus (1920), the modification mainly consisting in the size

of the gas sample which was 10 cc instead of 50 cc, which sample could be analysed with an accuracy of 1 cmm or .001 %. Only CO_2 determinations were carried out, the oxygen was not considered.

The experimental arrangement is half-schematically represented in fig. 1, the explanation of which is as follows.

The algae are placed in the assimilation vessel 15. Through this vessel

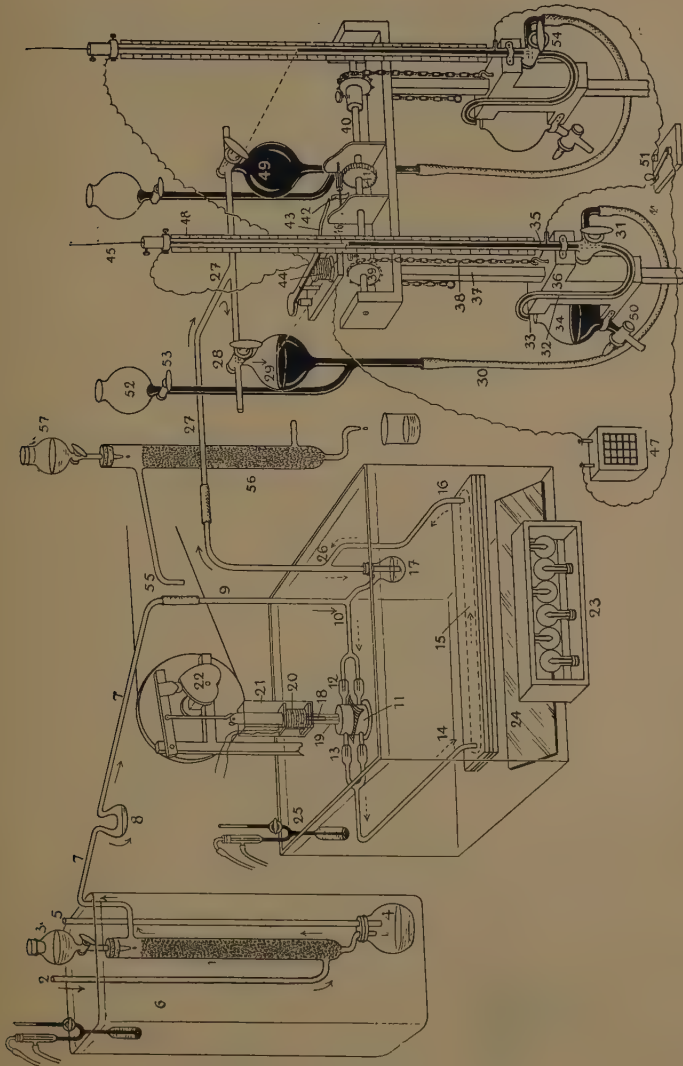


Fig. 1.

an air current passes. This air has passed through the CO_2 generator 1, in which it has been supplied with a constant, known amount of CO_2 .

The air which leaves the assimilation vessel is collected above mercury in the aspirator 29. This mercury is running out of the aspirator with constant velocity. Air samples are taken from this aspirator and analysed.

If the above mentioned air current should enter the assimilation vessel at 14 and should leave it at 16, a considerable gradient in CO_2 concentration from 14 to 16 should exist; the concentration would not be the same in different parts of the vessel. For this reason circulation has been applied, the air being thoroughly mixed by means of a circulation current of much greater velocity than the supply current. By this means a minimal gradient of CO_2 concentration is obtained in the assimilation vessel.

The supply current as well as the discharge current are indicated in fig. 1 by drawn arrows, the circulation current is indicated by dotted arrows.

As it proved impossible to install the circulation apparatus inside of the assimilation vessel, it has been mounted outside the vessel as a small suction-pressure pump 11, which immediately drags along in a swift current all CO_2 containing air, which enters the system at 10.

After having entered, the CO_2 is partly used by the algae in 15, the remainder is carried off at 26. The air, which leaves the system at 26 has the same CO_2 concentration as the air in the assimilation vessel; the assimilation in cmm CO_2 per hour is computed from the difference in concentration of entering and discharged air.

The generator consists of a long glass tube 1, filled with small glass beads. An aqueous solution of Na_2CO_3 and NaHCO_3 (in definite proportion, together .5 grammol p. L.) drips from vessel 3 into the generator. This solution is discharged into vessel 4, which may be emptied from time to time by siphoning through tube 5. This complex is placed into thermostat 6, in which the water is kept very accurately at 30°C . by means of a microburner and a toluene regulator.

The air enters the generator by tube 2 and passes unhampered through the openings between the beads, by which the solution drips down, (principle of countercurrent). The air is in equilibrium with the solution when it leaves the generator.

For air, in equilibrium with such a solution of Na_2CO_3 and NaHCO_3 , has at a certain temperature, a definite CO_2 concentration. For several mixtures of different proportion of both salts, this CO_2 concentration has been determined at 30°C . by a number of gasanalyses.

| | | | | | |
|--------------------------|--------------|-------|-------|-------|-------|
| Na_2CO_3 | grammol p.L. | 0.325 | 0.259 | 0.182 | 0.126 |
| NaHCO_3 | „ p.L. | 0.175 | 0.241 | 0.318 | 0.374 |
| CO_2 | vol % | 0.090 | 0.204 | 0.497 | 1.006 |

In the entrance tube 7 a small reservoir 8 has been blown, which contains a few drops of acidulated 25 % NaCl solution, in order to lower the

vapour tension of the air to prevent the formation of condensation water at other places of the system.

The *circulation pump* 11 consists of two small cylinders, between which a rubber membrane is clamped. At both sides of each cylinder there are small valves 12 and 13, which only admit the air in the direction right to left. The centre of the membrane is connected to a rod, which supports at its upper end a small piece of iron 18, enclosed within a small glass tube 19, which is sealed at the top.

The rotation of the cordate-shaped disc 22 causes the electric spool 20 to move upwards and downwards around tube 19. This movement induces a similar movement in the small piece of iron, which, transmitted to the membrane, causes the pump to function. The electric spool is protected from the water in the thermostate by the cover 21, which is shown transparent in the figure.

The electromagnetic device was necessitated by the great permeability of rubber for CO_2 . A rubber membrane in one-side contact with atmospheric air or with water allows a considerable diffusion of CO_2 , which would cause a loss of this gas by leakage.

In the pump, described above, the power transmission takes place through glass, which is permeable to magnetism but not permeable to CO_2 . For the same reason the rubber connections of the glass tubes throughout the system were made such as to secure contact between the glass tubes.

The *assimilation chamber* 15 consists of two glass plates (bottom and lid), between which is pressed a rubber ring $\pm .8$ mm. thick. The height of the assimilation chamber is therefore .8 mm.

The rubber ring was cut from the inner tube of a bicycle tire. The thin layer of algae rests on the bottom of the chamber.

The *illumination* (23) takes place by means of 1—6 lamps of 50 candlepower (Philips $\frac{1}{2}$ Watt 6—8 volt automobile lights) which burn on a storage battery.

The voltage may be regulated by means of a variable resistance. In this way the light intensity is kept constant to about 1 %. For higher intensities I used a Philips projection lamp (± 1650 candlepower) the intensity of which is obviously more variable, with the fluctuations in the city-current.

The light is projected perpendicularly from below upon the algae by means of a mirror; other light is screened off by means of black paper.

The assimilation chamber and the circulation apparatus are mounted together on a frame made of copper, well plated with nickel. This frame can be put in the thermostate 25, in which the temperature can be changed arbitrarily by adding warm or cold water. Within 15 minutes the temperature may be made constant up to about $.1^\circ \text{C}$. by means of a microburner and adjustable toluene regulator.

To the circulating apparatus belongs a small gas washing bottle 17, containing a small amount of distilled water. By observing the air bubbling

through it, the rate of the circulating current may be controlled. In this way the water vapour tension of the air is kept saturated and the dessiccation of the algae is prevented.

The air leaves the circulation apparatus at 26 and enters the aspirator through the tube 27.

The aspirator regulates the rate of the supply and discharge current by means of mercury, which is running out of the glassvessel 29. Through the entire system of tubes the air in this vessel is at 2 in free communication with the atmospheric air. The rate at which the air enters the vessel 29 is the same as the rate at which it is sucked into the generator at 2, enters the circulation apparatus at 10 and leaves it at 26.

The mercury has to be run out at a constant and adjustable velocity. This is attained in the following manner. The mercury flows successively through the rubber tube 30, the three-way tap 31 and the capillary glass tube with a very narrow part 32, where the current meets a strong resistance. Finally it drops at 33 in the vessel 34, in which it is collected.

The rapidity of this mercury current is determined: 1° by the height of the mercury column above the opening 33, 2° by the constant resistance in 32.

When the mercury level in 29 is going down the rapidity of the current will diminish, unless the opening 33 is going down at the same rate. This is attained by the following automatical device. At the three-way tap 31 a capillary tube 35 is attached, forming communicating vessels with 29. So in 29 and 35 the mercury meniscus is at the same level.

The capillary tube 35, the tap 31, the resistance tube 32 and the receptacle 34 are mounted together on a log of wood 36, which can be moved along the bar 37 and is suspended by a chain 38. This chain is hanging on a cogwheel, that can be fixed with a screw on the spindle 40. By turning this spindle, the wing 42 is brought in a swift turning movement by means of a number of cogwheels 41 (only two of them are given in the figure). This wing (and the spindle with it) is stopped, when the lever 43 is pulled down. This occurs when a faint electric current passes the electromagnet 44.

In the capillary tube 35 a piece of iron-wire 45, provided with a tiny platinum needle 46, is put from above. If this needle comes into contact with the mercury, a current from the accumulator 47 passes the electromagnet 44, causing the wing 42 and the spindle 40 to be fixed. If subsequently the mercury level in 29 (and therefore also in 35) is going down, the contact with the platinum needle is broken, the wing is released and the log 36 begins to move slowly downward, causing a swift movement of the wing. When the platinum needle reaches the mercury again, the movement is stopped at once.

In this way the mercury level is kept at a constant height above the opening 33. This height is determined by the position of the platinum needle in the capillary tube 35, which can be read off on a scale 48. To

each position corresponds a certain height of the mercury column and therefore a certain rate of the current; for a number of positions throughout the scale the corresponding rate of the current has been tested empirically. So the rapidity of the mercury current can be regulated at will from 0 to 160 cc an hour, accurate to $\frac{1}{2}$ % at the mean velocities.

At the beginning of an experiment the CO_2 content of the air, entering the aspirator 29, has not yet become constant. Not before a volume of air, four times as great as the content of the circulation system (this is about 17 cc), has been sucked through, an equilibrium has been established between supply, consumption and discharge of CO_2 . The CO_2 content of the discharged air thus being constant, this air may now be used for analysis.

Therefore the current of air is conducted to a second aspirator 49, provided with the same arrangement as the former one and adjusted at the same velocity of mercury current, after some manipulations the air current may be diverted from 29 to 49 in a single moment, without interruption, by opening tap 54 and closing tap 31 at the same time.

The air in the aspirator 29 now may be discharged. Therefore the mercury is run out of tap 50 and poured into the receptacle 52. Subsequently tap 28 is opened to the left and by opening tap 53 the mercury runs back into aspirator 29, driving out the air.

When determining the respiration, I mostly used air containing no CO_2 . For that purpose tube 9 is connected with tube 55 of generator 56; through this generator a 2 % KOH solution drips from vessel 57 along a number of small glass beads. From the air, passing between the beads in opposite direction, the CO_2 is absorbed.

The experiments.

By assimilation is meant the CO_2 consumption under illumination to which is added the CO_2 production in the dark.

In order to obtain comparable values under different conditions, the values obtained in the experiments have to be reduced to a certain unity of living material. Usually this is 1 gram of dry weight.

In my experiments, however, the quantities used were extremely small (1—3 m.gr.) and could not be weighed with sufficient accuracy. So I have chosen another unity, to wit the quantity which assimilates 100 cc CO_2 an hour at certain, well defined conditions. These conditions are: excess of CO_2 , illumination by 6 lamps (light intensity 6.18) and temperature 20°C . At those conditions the temperature is limiting factor. By preliminary experiments it was shown that the CO_2 concentration was in excess (that means without influence on the velocity of assimilation) when more than .040 vol. % CO_2 was present.

The unity of material in question contains upwards of 40 m. of cell threads and is weighing about 1 m.gr. when dried at the air.

During the experiments, which often took a long time, the living material increased by growth. Small corrections were to be applied for it.

The influence of the light intensity. The intensity of each separate lamp was tested by using the algae themselves as a photometer. At the low intensity of one lamp the light is limiting factor and the assimilation is directly proportional to the light intensity. The intensity of one of the lamps was arbitrarily taken as unity and the intensities of the other lamps expressed in terms of this unity.

Fig. 2 is a graph representing the influence of the light intensity on the assimilation velocity at 20° C. and the CO₂ concentration in excess. The

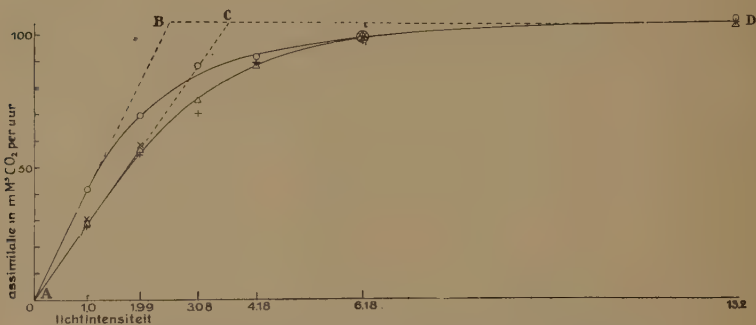


Fig. 2. The relation between the light intensity and the assimilation rate (cmm per hour).

marks +, Δ and \times are representing three experiments with algae grown upon a fresh culture medium. The marks O indicate an experiment with algae upon an old, exhausted medium. As the results are different in those two cases, the algae are to be cultivated in constant conditions in order to obtain comparable results. Therefore I took care to use only material on fresh culture media.

As fig. 2 shows, the maximal assimilation velocity at 20° C. is nearly reached, when illuminating with 6 lamps (light intensity 6.18), for doubling this intensity results in an increase of 5 % only.

The figure also shows that in normal cases the assimilation velocity is directly proportional to the light intensity up to 1.99 (for up to this intensity the curve is a straight line). Therefore at this intensity the light is still limiting factor.

The influence of the temperature. At a high intensity of light (6.18) and excess of CO₂ a Q₁₀ of 1.87 was found between 12° and 20° C.

At a low intensity of light (1.0) and the same temperature interval a Q₁₀ = 0.90 was found, not much differing from unity.

The influence of the CO₂ concentration. As has been pointed out, all values are reduced to a quantity of algae, which assimilates 100 cmm CO₂

an hour at a light intensity of 6.18 and a temperature of 20° C. As one may see at fig. 2 the same quantity assimilates 57 cmm CO₂ an hour at a light intensity of 1.99. The experiments about the influence of temperature showed, that at 12° C. and a light intensity of 6.18 this same quantity of algae assimilates 61 cmm CO₂ an hour, of course with CO₂ in excess.

These facts were used to calculate the experiments about the influence of the concentration of CO₂ (see fig. 3).

These experiments were started with an excess of CO₂, there-upon the CO₂ concentration was decreased till it became limiting factor, to establish its influence on the assimilation rate. This was done under three different conditions, viz.

1°. at 20° C., light intensity 6.18 (fig. 3, O)

2°. „ 12° C., „ 6.18 (fig. 3, +)

3°. „ 20° C., „ 1.99 (fig. 3, Δ)

In this way the influence of light and temperature was established in that part of the curve, where the CO₂ concentration is limiting factor. As may be seen in fig. 3, this part is a straight line nearly to the transition

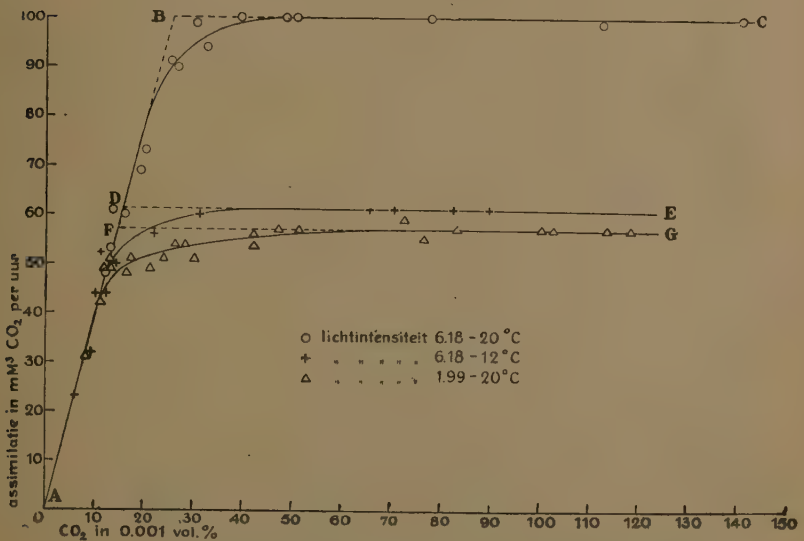


Fig. 3. The relation between the carbon dioxide concentration (expressed in units of .001 volume per cent of the air) and the assimilation rate (cmm per hour) at different conditions of temperature and light intensity.

point. In this part temperature and light intensity are obviously without any influence on the assimilation velocity (as far as the accuracy of the experiments allows to conclude); for here (on the line AF) the curves

for high and low light intensity as well as for high and low temperature coincide altogether.

Discussion of the Results.

Examining the results in connection to what was said in the first pages, it is clear that BLACKMAN's formulation gives a rather good description of the assimilatory behaviour of the single cell. In the figures 2 and 3 the "ideal BLACKMAN curves" are indicated by dotted lines; the greatest deviation shows fig 2, where it amounts 25 to 30 % (points *B* and *C*). I might ascribe it to the fact that, even in a single chloroplast, a considerable amount of light is absorbed. So the intensity of light is not the same at the different parts of the chloroplast. At decreasing intensity the light will therefore not become limiting at the same time in the different parts of the plastid. The same objection, which is valuable for leaves to such a great extent, seems not to be quite eliminated here.

This curve, however, agrees considerably better with BLACKMAN's scheme than the curve obtained by WARBURG (1919) with *Chlorella*. So I might conclude that in WARBURG's experiments a part of the algae is shadowed by the others.

The curves in fig. 3 show a nearly ideal BLACKMAN scheme. The deviations in the transition points *B*, *D* and *F* are upwards of 10 %. Probably those deviations are partly due to the different carbon dioxide supply in the different parts of the chloroplasts, causing an earlier CO₂ limitation in one part than in the other.

How are the above mentioned facts to be explained? Will it be possible to reduce the assimilation to a catenary process?

The answer upon these questions can be in the affirmative, when the assimilation is assumed to consist of: 1^o. a diffusion process, by which the CO₂ is transferred from the external medium into the chloroplast, 2^o. a photochemical process, 3^o. a dark chemical process.

Each of these consecutive processes may determine separately the rate of the assimilation, when 1^o. the concentration of CO₂, 2^o. the intensity of the light, 3^o. the temperature are limiting factor.

When this holds good, the three processes must possess the three combinations of properties, mentioned at the beginning of the article.

The velocity of a diffusion process is *ceteris paribus* directly proportional to the difference of the concentrations at the beginning and the end of the path along which diffusion is proceeding. When the CO₂ concentration is 0 at the end — inside the chloroplast — the diffusion velocity will be directly proportional to the concentration at the beginning of the path — outside the cell. Such a linear dependency shows the line *A F B D* in fig. 3.

Of course the light does not affect this process. However one should expect an influence of the temperature, as a Q_{10} of 1.2 to 1.3 is generally mentioned for diffusion processes.

On second thought this consideration is not correct. We may consider the cellwall and the protoplasm, through which the CO_2 is diffusing, as a water-like medium. Before entering the cell, the CO_2 has to dissolve into the outmost layer of the cellwall.

It is highly probable that in this outmost layer the CO_2 concentration is in equilibrium with that of the adjacent air. The solubility of CO_2 in water, however, decreases with increasing temperature. When this change of solubility is taken into account, from the apparent $Q_{10} = 1$ as found in my experiments a real $Q_{10} = 1.3$ can be deduced.

Still another argument may be mentioned. It was possible to measure approximately the total length of the cell threads used in some experiments, and to calculate the total surface available to the penetration of the CO_2 .

This surface was about 69 cm for the said unity of cell material. Since the velocity of the process and the difference of concentration are given, one may calculate, by means of the diffusion constant of CO_2 in water, the thickness of a water layer offering the same resistance to diffusion as the cells do.

This appears to be 8μ . Now the cells have a thickness of about 8μ and the chloroplasts are 4μ thick at some places. Since it is highly probable that in the cell wall and the protoplasm the CO_2 has a smaller diffusion constant than in water, the accordance may be called satisfactory.

I do not agree with the opinion of WARBURG, who believes that in *Chlorella* the resistance to diffusion of CO_2 may be neglected, the more so as in WARBURG's experiments the CO_2 becomes limiting at about the same concentration as in mine.

As was argued herebefore, the diffusion velocity is directly proportional to the CO_2 concentration outside the cell, as long as the concentration inside the cell remains 0. Conversely when accepting that we have to do with a diffusion process, we can say that the CO_2 concentration inside of the cell remains 0, as long as there is a rectilinear dependence and that this concentration increases above 0, as soon as the rectilinear dependence ceases. Now fig. 3 shows that the deviation from the straight line *AB* begins only when the maximal assimilation velocity is nearly reached.

At a CO_2 pressure inside the cell, corresponding to .001 % CO_2 in the air, the assimilation is already functioning at nearly full speed. One is forced to accept that on the spot, where the reaction, subsequent to the diffusion proceeds, nearly a maximal amount of CO_2 is already available.

Obviously the assimilatory agent (either chlorophyll or an enzyme) has an enormous affinity to CO_2 , being able to saturate itself almost quantitatively with CO_2 , even at a pressure of .001 % or $\frac{1}{100000}$ atm.

The rate of the photochemical process, governing the assimilation velocity when the light is limiting factor, is directly proportional to the light intensity, according to the laws of photochemistry. With many photo-

chemical processes in vitro it has in common a $Q_{19} = 1$, as pointed out by several authors. The independence of the concentration of CO_2 needs no further explanation, after what has been said above about the assimilatory agent.

About the dark chemical reaction of the catenary process much has been written. Little is known, however, about its nature. The expressions "Blackman reaction" (WARBURG) and "enzymic factor" (WILLSTÄTTER and STOLL) refer to this reaction. It is a non-photochemical process, so the light does not affect it. It has a high, "chemical" temperature coefficient. As for the CO_2 , this probably does not take part in it, but a reaction product of the photochemical process. Consequently it is independent of the CO_2 concentration.

As a summary we may say, that it is possible to study three parts of the assimilatory mechanism separately, without interfering with the organisation of the cell, only by altering the environmental factors.

Finally I determined the so-called *assimilation number* of Hormidium. WILLSTÄTTER and STOLL defined it as the amount of grams CO_2 , assimilated per hour, divided by the amount of grams chlorophyll.

I determined the chlorophyll content of my algae spectrophotometrically, according to a method of WEIGERT (1916) by means of a "Color Analyser" of KEUFFEL & ESSER Co. This instrument was kindly given at my disposal by Prof. Dr. N. SCHOORL. As an average of five determinations I obtained an assimilation number of 6.75 at 20°C . and a lightintensity of 6.18.

The above-said unity of cell-material contained on an average .0271 m.g. of chlorophyll.

LITERATURE.

1. W. BENECKE: Beiträge zum Problem der Kohlensäureassimilation. Zeitschr. f. Bot. **13**, p. 417. 1921.
2. F. F. BLACKMAN: Optima and Limiting Factors. Annals of Botany **19**, p. 281. 1905.
3. P. BOYSEN JENSEN: Studies on the Production of Matter in Light- and Shadow-Plants. Botanisk Tidsskr. **36**, p. 219. 1919.
4. G. E. BRIGGS: The Development of Photosynthetic Activity during Germination. Proc. Roy. Soc. London **91**, B, p. 249. 1920.
5. W. H. BROWN and G. W. HEISE: The application of Photochemical Temperature Coefficients to the Velocity of Carbon Dioxide Assimilation. Philippine Journ. of Sc. C. Bot. **12**, p. 1. 1917.
6. R. HARDER: Kritische Versuche zu BLACKMAN's Theorie der begrenzenden Factoren bei der Kohlensäureassimilation. Jahrb. f. wiss. Bot. **60**, p. 531. 1921.
7. T. H. VAN DEN HONERT: Koolzuurassimilatie en Beperkende Factoren. Doctor's Thesis, Utrecht, 1928.
8. AUG. KROGH: A Gasanalysis Apparatus accurate to 0.001 % etc. Bioch. Journ. **14**. 1920.
9. H. LUNDEGÅRDH: Der Kreislauf der Kohlensäure in der Natur. Jena, 1924.
10. H. SCHROEDER: Die Kohlendioxydversorgung der Chloroplasten. Flora **117**, N.F. **17** p. 270. 1924.
11. D. THODAY: Carbon Assimilation, South African Journ. of Sc. **19**, p. 52. 1922.
12. O. WARBURG: Ueber die Geschwindigkeit der photochemischen Kohlensäure-zersetzung in lebenden Zellen I. Bioch. Zeitschr. **100**, p. 230. 1919.

13. O. WARBURG: Ueber die Geschwindigkeit der photochemischen Kohlensäure-zersetzung in lebenden Zellen II. Bioch. Zeitschr. 103, p. 188. 1920.

14. O. WARBURG: Theorie der Kohlensäureassimilation. Naturwissenschaften 9, p. 354. 1921.

15. O. WARBURG und T. UYESUGI: Ueber die BLACKMANsche Reaction. Bioch. Zeitschr. 146 p. 486. 1924.

16. F. WEIGERT: Ueber Absorptionsspectren und über eine einfache Methode zu ihrer quantitativen Bestimmung. Ber. d. d. Chem. Ges. 49, I, p. 1497. 1916.

17. R. WILLSTÄTTER und A. STOLL: Untersuchungen über die Assimilation der Kohlensäure. Berlin, 1918.

Utrecht, March 1928.

Botanical Laboratory.

CORRIGENDUM.

In the title of Dr. A. P. TIMMER's paper (these Proceedings, p. 780, and at the heading of the adjoined plates, erroneously has been printed: mit links-seitiger zerebraler Atrophie, instead of: mit *links-seitiger zerebellärer Atrophie*.

In Prof. L. E. J. BROUWER's article *Zur Geschichtschreibung der Dimensionstheorie* (these Proceedings Vol. 31) p. 957, line 5—6 the words: auf dem Umschlage der Monatsh. f. Math. u. Phys. 34 und are to be struck out.

ERRATUM.

Proceedings Kon. Akad. v. Wetensch., Amsterdam, 31, p. 1060, Table I

for: "97" read: "79".

for: "94" read: "76".
